Process Development and Scale-Up of Advanced Active Battery Materials

Ozge Kahvecioglu Feridun (PI)

Argonne National Laboratory
Project ID: BAT167

June 11, 2019

OVERVIEW

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2019
- Percent complete: on going

Budget

- Total project funding:
  - $1.2M in FY18
  - $1.2M in FY19

Barriers

- Cost: Reduce manufacturing costs with scalable continuous processes
- Availability: Advanced cathode materials needed for research are not commercially available with the desired composition or morphology

Partners

- Collaborators in Deep-Dive into Next-Generation Cathode Materials (BAT375)
  - ANL, ORNL, NREL, LBNL, PNNL
- Thick, Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing (BAT164)
  - Oak Ridge National Laboratory
- Small NCM particles that are not commercially available
  - Volexion: for enabling graphene coating
  - Blue Current: for enabling all-solid-state battery development

OBJECTIVES AND RELEVANCE

- The objective of this program is to provide a systematic research approach to:
  - Produce and provide **sufficient quantities of high quality** battery materials for industrial evaluation and to support further research
  - Evaluate **emerging synthesis technologies** for the production of experimental battery materials
  - Develop **cost-effective, scalable** processes for manufacturing of advance materials that are not commercially available
- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between invention of new advanced battery materials, market evaluation of these materials and high-volume manufacturing
  - Reducing the risk associated with the commercialization of new battery materials
- This program provides large quantities of materials with consistent quality
  - For industrial validation and prototyping in large format cells
  - To allow battery community access to new materials and advance further research

APPROACH AND STRATEGY

- Basic science researchers invent new materials, synthesize small amounts and evaluate electrochemical performance in small cell formats
- Materials Engineering Research Facility (MERF) collects information about new materials, prioritizes them based on level of interest, validates performance and scale up feasibility
- MERF evaluates new emerging manufacturing technologies, conducts process R&D, develops and validates optimal process parameters for production of new materials
- Proof of concept in stages from 10g to 100g to kg's
- Make new materials available to assist basic researchers and to facilitate industrial evaluation
- Provide feedback to discovery scientists helping promote future research
- The program evaluates emerging synthesis techniques that can reduce costs

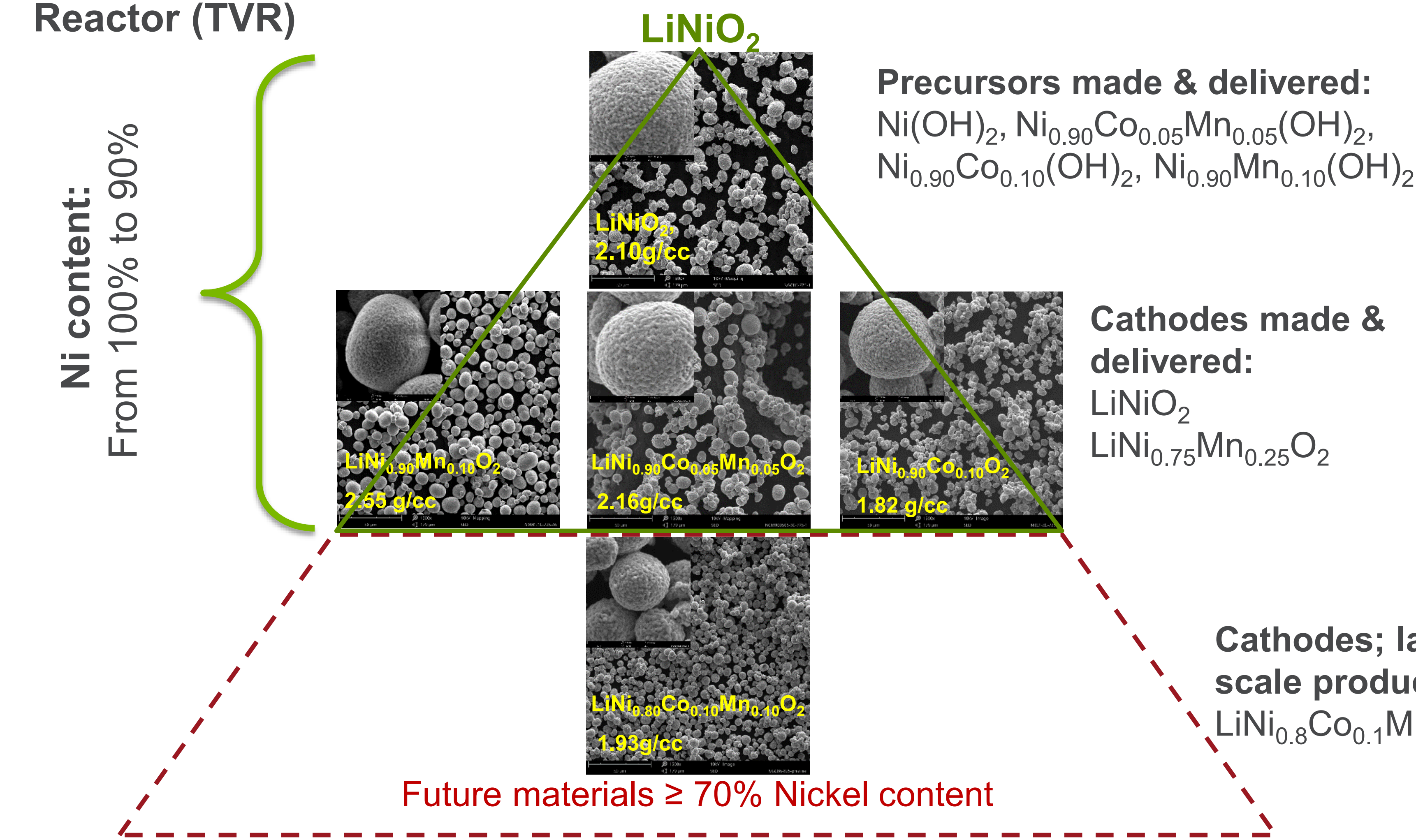
APPROACH - MILESTONES

- FY 19 - Materials produced and provided in support for:
  - Deep-Dive into Next-Generation Cathode Materials:
    - Hundreds of grams of precursors: $Ni(OH)_2$, $Ni_{0.90}Co_{0.05}Mn_{0.05}(OH)_2$, $Ni_{0.90}Co_{0.10}(OH)_2$, $Ni_{0.90}Mn_{0.10}(OH)_2$ → calcination optimization were done for respective cathodes
    - Hundreds of grams of cathodes: $LiNiO_2$, $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$, $LiNi_{0.90}Co_{0.10}O_2$, $LiNi_{0.90}Mn_{0.10}O_2$, $LiNi_{0.75}Mn_{0.25}O_2$
  - Small NCM Particles (D_{50} between 4-8 μm):
    - The materials below were provided to Volexion to enable their proprietary graphene coating technology
      - $LiNiO_2$
      - $LiNi_{0.80}Co_{0.10}Mn_{0.10}O_2$
      - $LiNi_{0.60}Co_{0.20}Mn_{0.20}O_2$
    - Small $LiNi_{0.80}Co_{0.10}Mn_{0.10}O_2$ & $LiNi_{0.60}Co_{0.20}Mn_{0.20}O_2$ materials were also provided to Blue Current @ 50 g scale per each
  - Taylor Vortex Reactor scalability evaluation for small particles:
    - In support for "Thick, Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing, (Jianlin Li, BAT164)"
      - 10 L TVR operation for $Ni_{0.80}Co_{0.10}Mn_{0.10}(OH)_2$ provided ~2.0 kg of material

TECHNICAL ACCOMPLISHMENTS

In support of "Deep-Dive into Next-Generation Cathode Materials" program

Target: Generate low(/no)-cobalt layered oxide cathodes using **Taylor Vortex Reactor (TVR)**



Precursors made & delivered:
$Ni(OH)_2$, $Ni_{0.90}Co_{0.05}Mn_{0.05}(OH)_2$, $Ni_{0.90}Co_{0.10}(OH)_2$, $Ni_{0.90}Mn_{0.10}(OH)_2$

Cathodes made & delivered:
$LiNiO_2$
$LiNi_{0.75}Mn_{0.25}O_2$

Cathodes; large scale production:
$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$

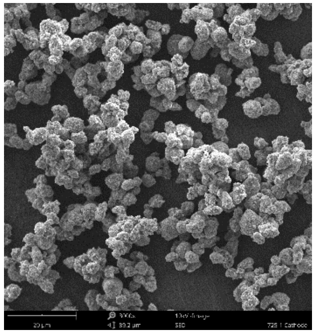
- Preliminary co-precipitation conditions with 1L **TVR** were utilized for six different compositions

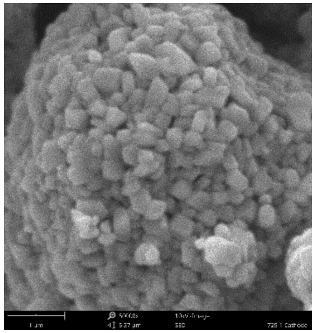
TECHNICAL ACCOMPLISHMENTS

Preliminary $Ni(OH)_2$ co-precipitation in 1L TVR

- Initial co-precipitation studies with 2 hours of residence time using 1L Taylor Vortex Reactor resulted in ~700 grams of yield with ~43g/h production rate
- The particles appeared (quasi-)spherical with a D_{50} of **4.8µm** in size

Preliminary $LiNiO_2$ cathodes

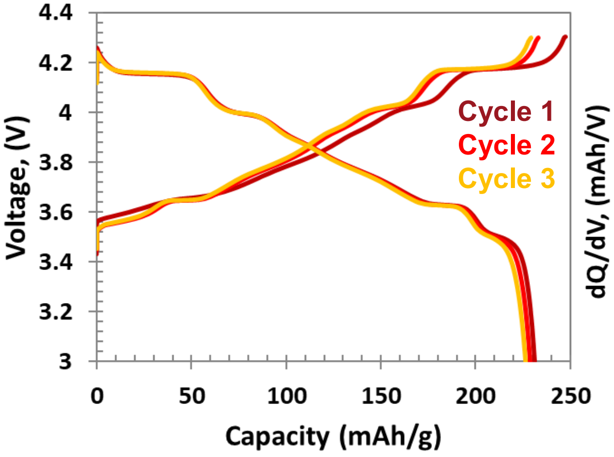


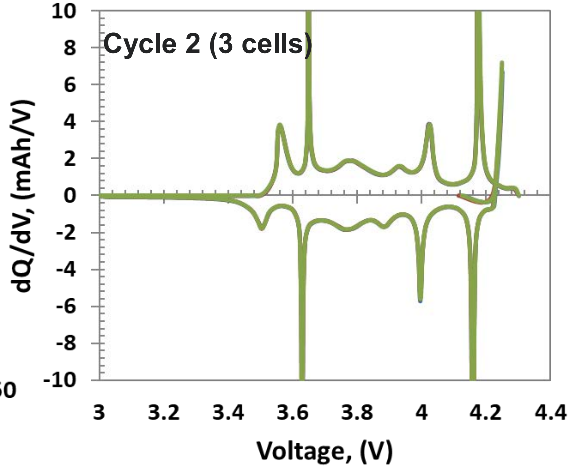


Calcination cond.; 725°C (hold for 4h) under O_2 flow

➢ Further optimization of TVR reaction recipe was made to achieve **≥ 10µm** size, spherical and denser particles

Electrochemical profile





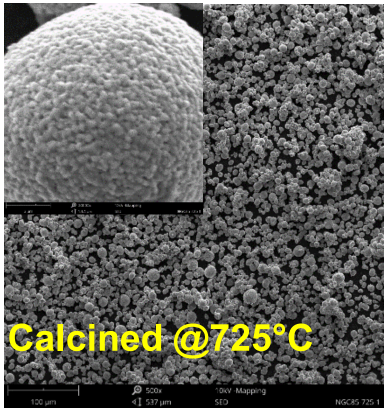
Sample	1st Cycle Efficiency (%)	1st Discharge (mAh/g)
725°C Li = 1.06	93.5	231

Electrolyte: 1.2 M $LiPF_6$ in EC/EMC (3:7)
Potential Window: 3.0 - 4.3 V @30°C

TECHNICAL ACCOMPLISHMENTS

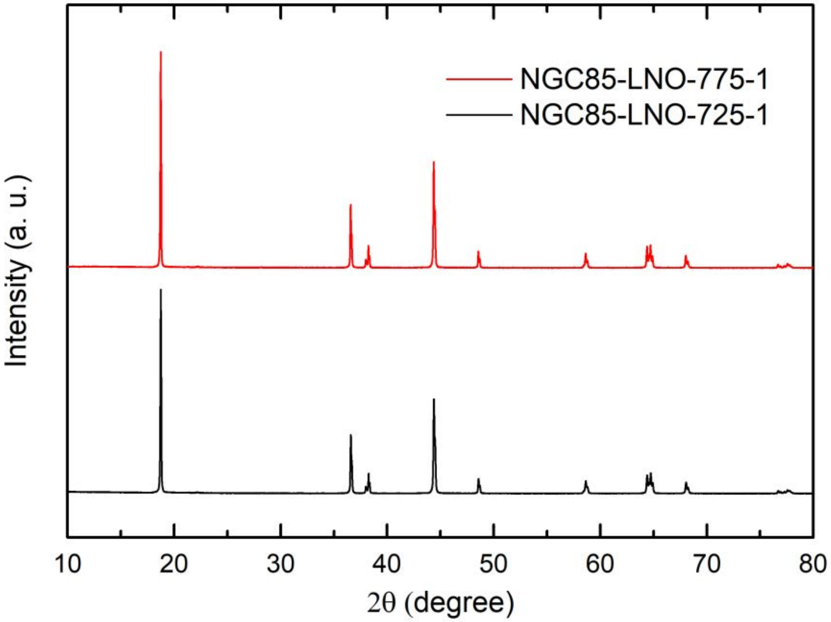
Synthesis of $LiNiO_2$

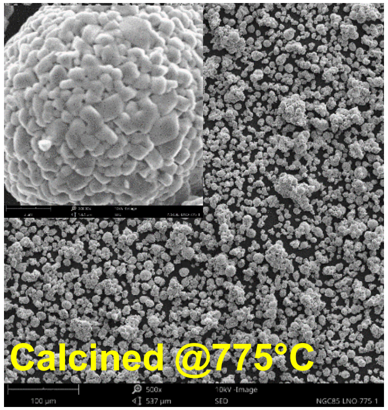
- Calcination optimization was carried out to adjust the Li ratio and to determine the optimal calcination temperature



Tap Density = 2.1 g/mL

- With the optimized co-precipitation recipe D_{50} of ~9 μm was achieved
- After calcination the D_{50} was ~12 μm





Tap Density = 2.08 g/mL

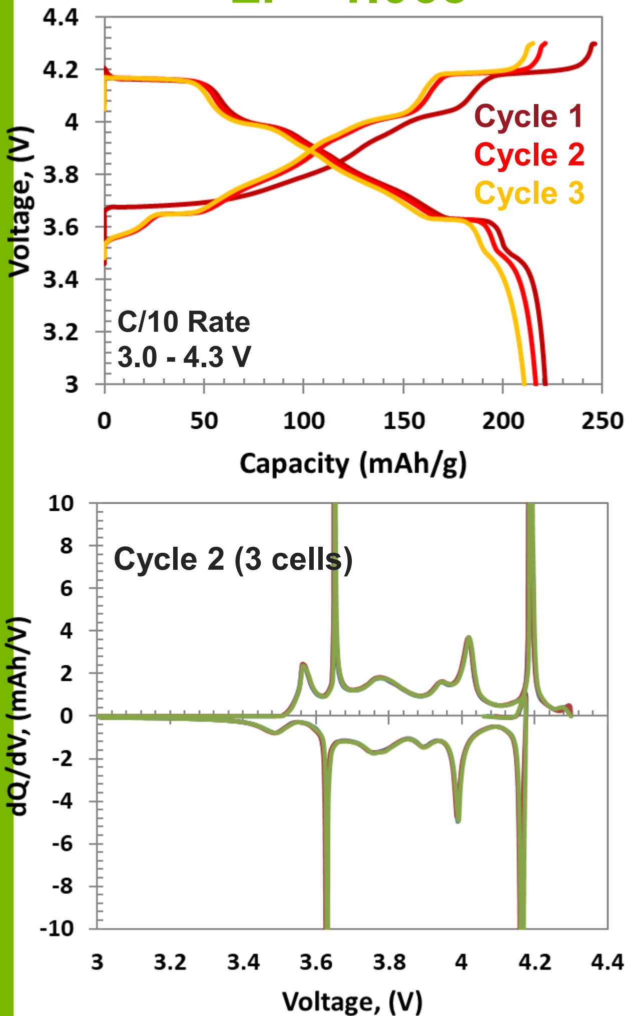
Sample	a (Å)	c (Å)	Ni/Li (%)	Crystallite size (μm)	Rw
NGC85-725-1	2.877	14.198	1.48	0.260	3.012
NGC85-775-1	2.878	14.197	2.01	0.282	3.745

- Phase pure, dense, crystalline and spherical cathodes
- Similar lattice parameters due to close calcination temperature

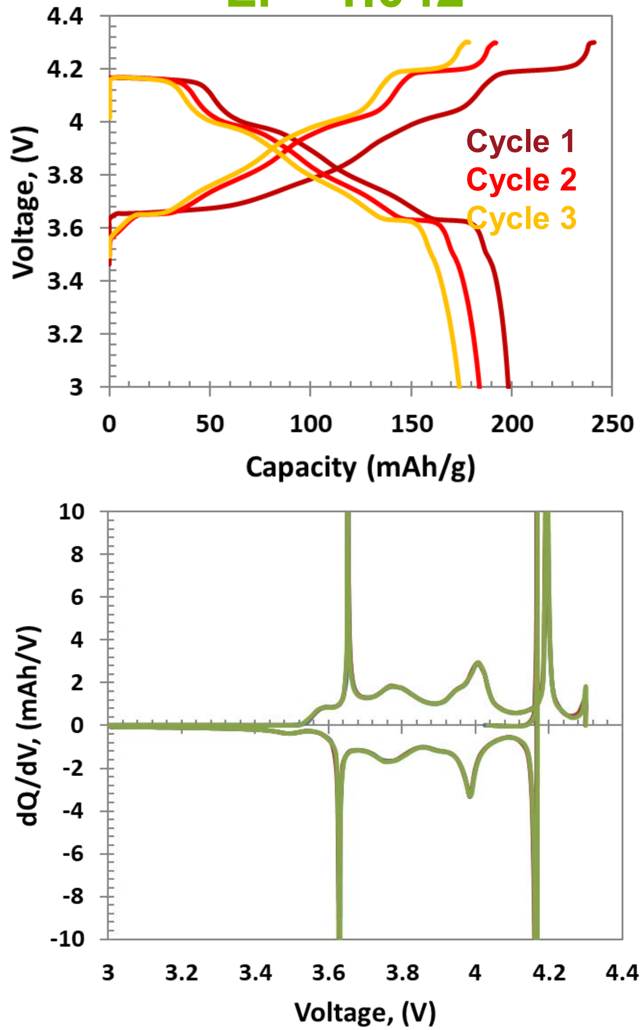
TECHNICAL ACCOMPLISHMENTS

Electrochemical Performance of $LiNiO_2$

725°C
Li = 1.063



775°C
Li = 1.042

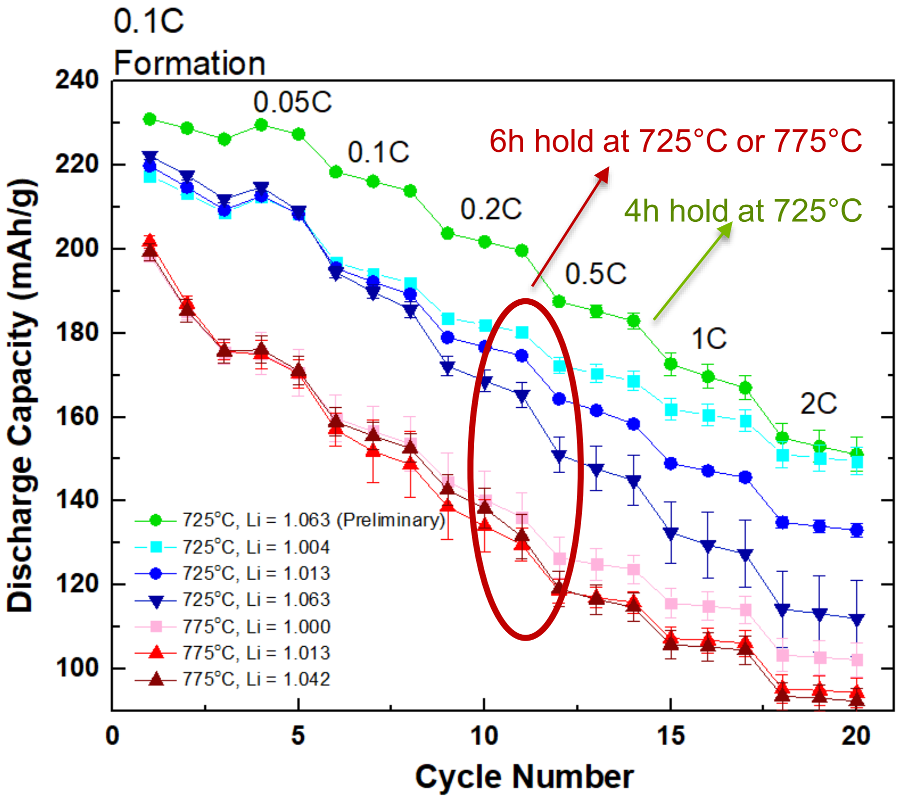


- Higher calcination temperatures result in lower capacity with faster capacity fade
- Multiple peaks in dQ/dV plots are characteristic in Ni-rich cathodes

Electrolyte: 1.2 M $LiPF_6$ in EC/EMC (3:7)
Potential Window: 3.0 - 4.3 V @30°C

TECHNICAL ACCOMPLISHMENTS

Electrochemical Rate Performance of $LiNiO_2$



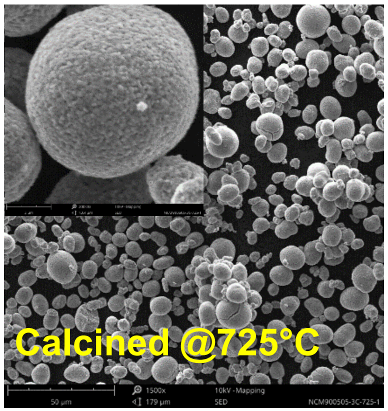
- Calcination conditions and the size & morphology of the particles plays an important role in the electrochemical performance
- Superior performance of cathode calcined at 725°C with shorter holding time

Sample	1st Cycle Efficiency (%)	1st Discharge (mAh/g)
725°C (Prelim.; ~**5µm**) Li = 1.063	93.5	231.0
725°C Li = 1.004	88.6	217.6
725°C Li = 1.031	89.1	219.9
725°C Li = 1.063	90.0	222.3
775°C Li = 1.000	82.5	198.5
775°C Li = 1.013	83.0	201.8
775°C Li = 1.042	82.6	199.3

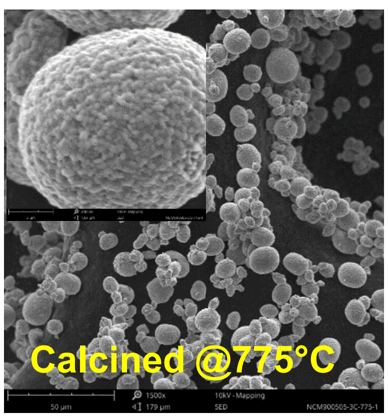
TECHNICAL ACCOMPLISHMENTS

Synthesis of $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$

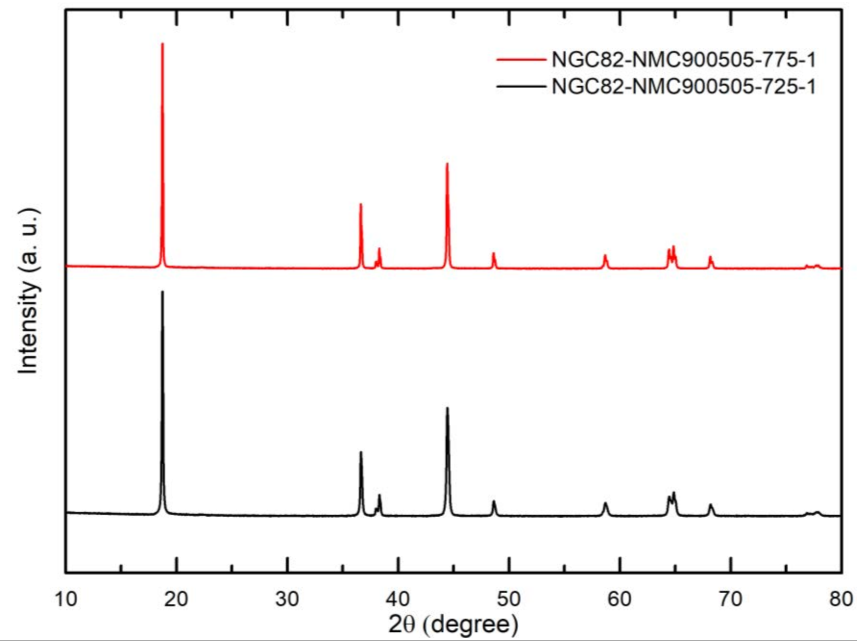
- Calcination optimization was carried out to adjust the Li ratio and determine the optimal calcination temperature



Tap Density = 2.21 g/mL



Tap Density = 2.16 g/mL



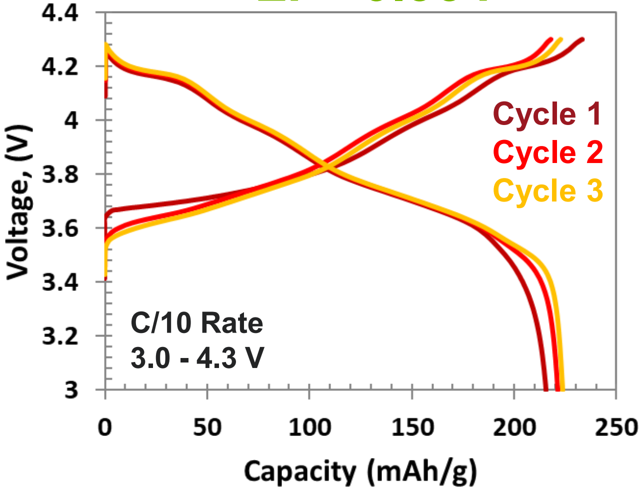
Sample	a (Å)	c (Å)	Ni/Li (%)	Crystallite size (µm)	Rw
NGC82-725-1	2.872	14.194	2.03	0.142	1.688
NGC82-775-1	2.873	14.197	1.19	0.237	2.208

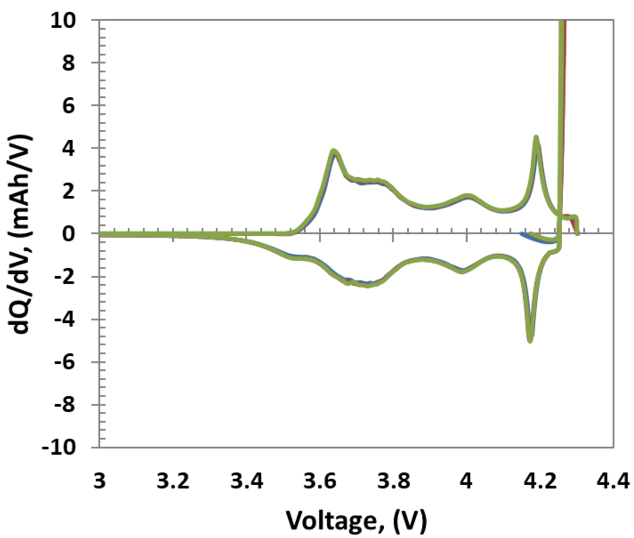
- Phase pure, highly crystalline, dense and spherical particles
- Higher calcination temperature reduces Ni/Li exchange

TECHNICAL ACCOMPLISHMENTS

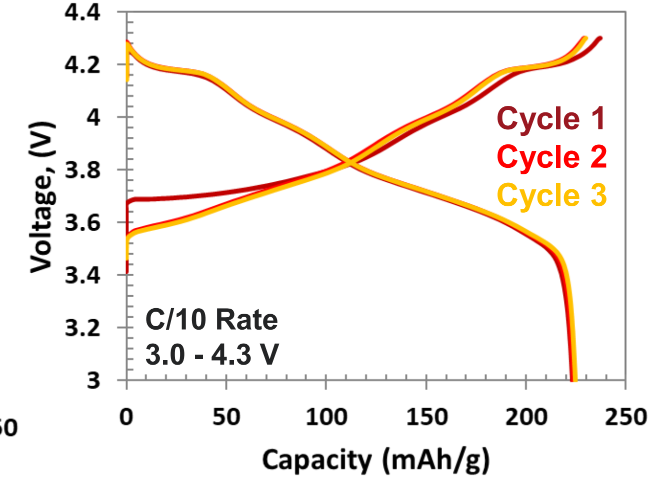
Electrochemical Performance of $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$

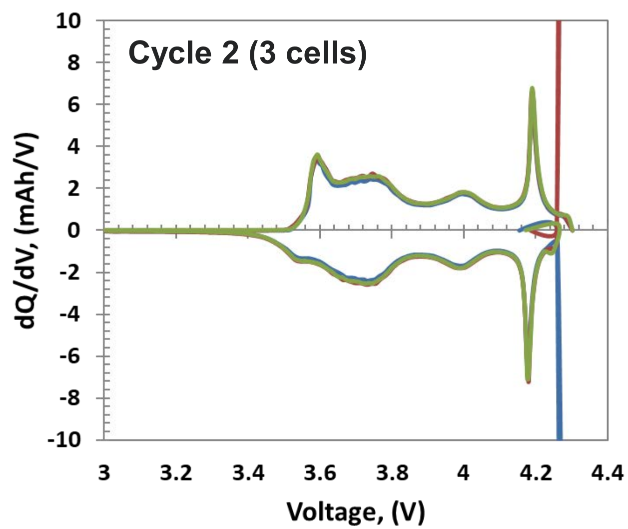
725°C (4)
Li = 0.991





775°C (4)
Li = 1.005



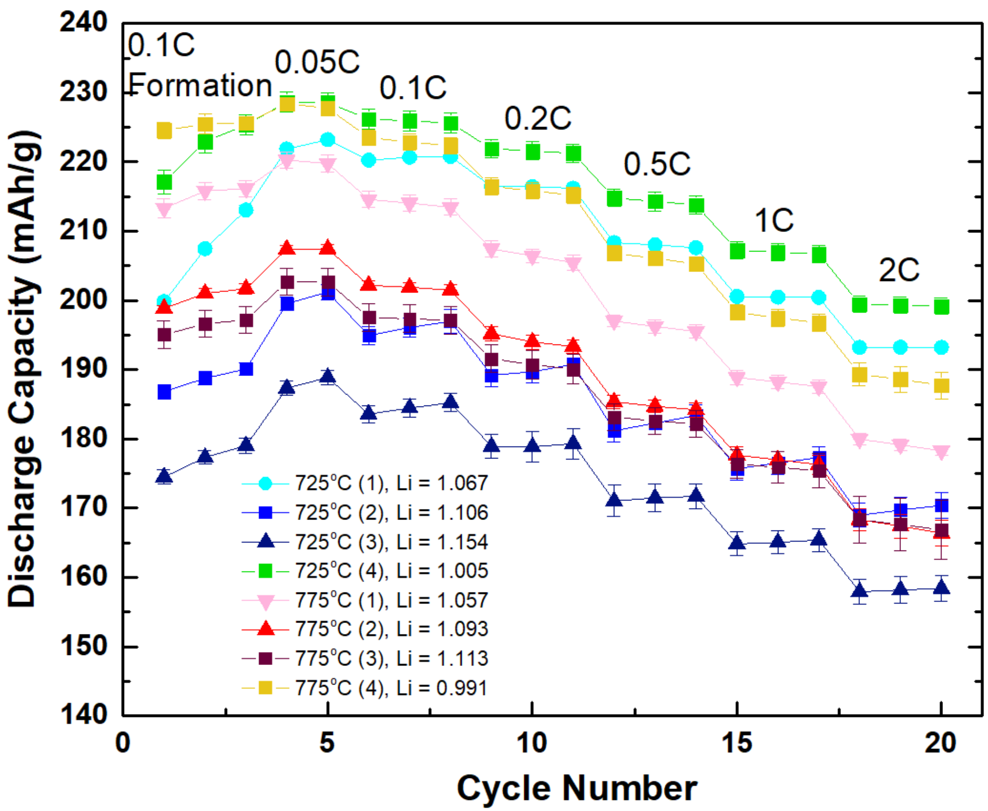


- Higher calcination temperature improves first cycle efficiency and results in higher initial discharge capacity
- Future optimization studies will investigate calcination temperatures at/above 800°C

Electrolyte: 1.2 M $LiPF_6$ in EC/EMC (3:7)
Potential Window: 3.0 - 4.3 V @30°C

TECHNICAL ACCOMPLISHMENTS

Electrochemical rate performance of $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$



Sample ID	1st Cycle Efficiency (%)	1st Discharge (mAh/g)
725°C (1) Li = 1.067	86.2	199.8
725°C (2) Li = 1.106	83.6	186.8
725°C (3) Li = 1.154	81.9	174.5
725°C (4) Li = 1.005	92.5	217.1
775°C (1) Li = 1.057	91.8	213.3
775°C (2) Li = 1.093	88.8	198.8
775°C (3) Li = 1.113	88.6	195.0
775°C (4) Li = 0.991	93.4	224.6

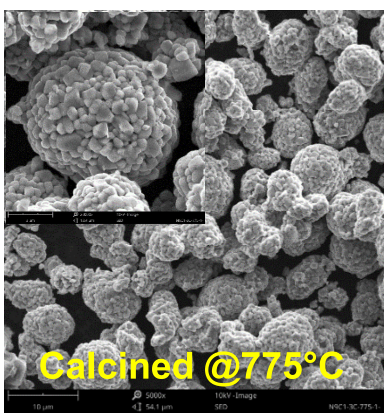
- Calcination temperature and Li-ratio play an important role for the electrochemical performance

TECHNICAL ACCOMPLISHMENTS

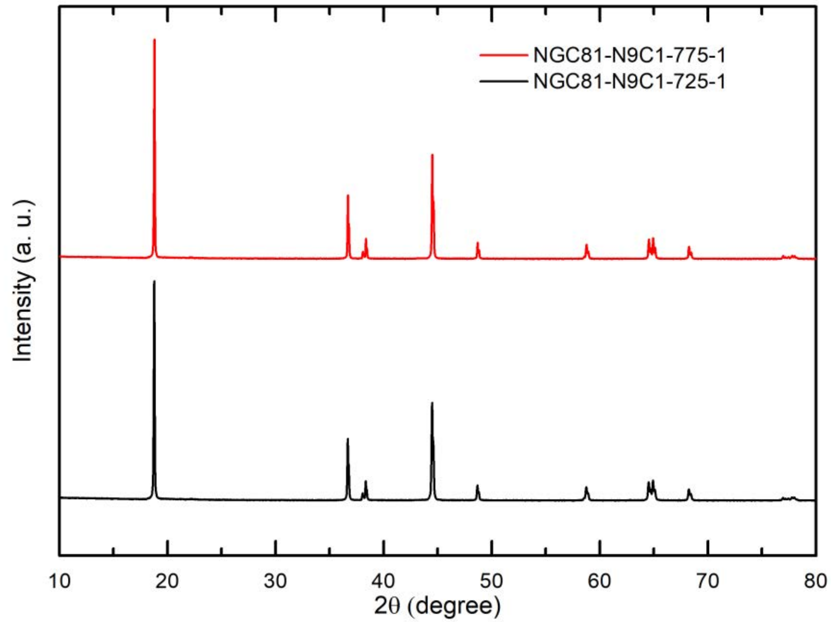
Synthesis of $LiNi_{0.90}Co_{0.10}O_2$

- Calcination optimization was carried out to adjust the Li ratio and to determine the optimal calcination temperature

Tap Density = 1.82 g/mL



Tap Density = 1.97 g/mL



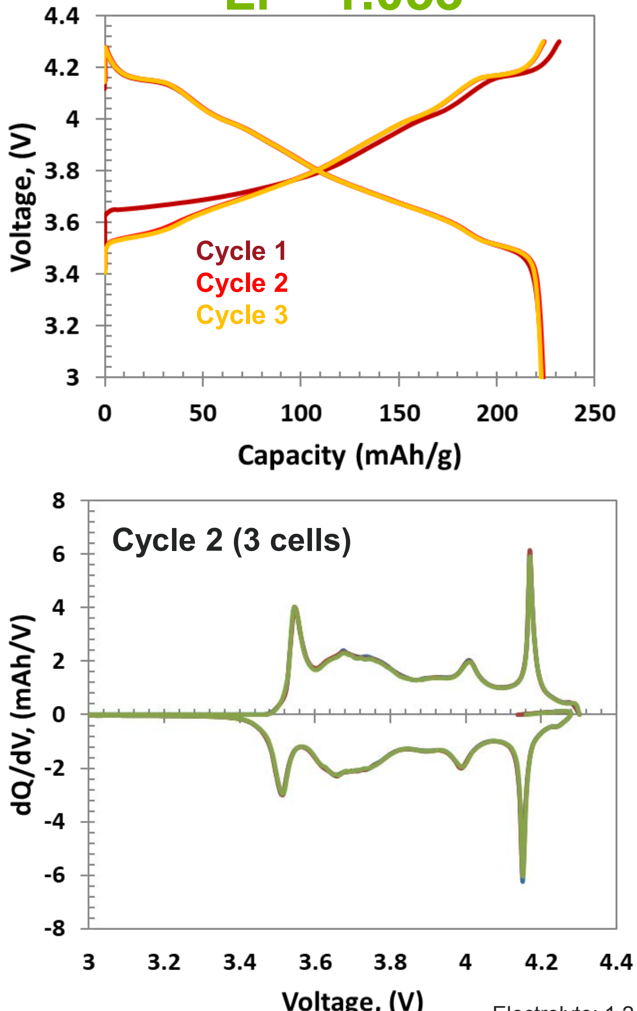
Sample	a (Å)	c (Å)	Ni/Li (%)	Crystallite size (μm)	Rw
NGC81-725-1	2.870	14.181	0.31	0.233	1.883
NGC81-775-1	2.870	14.178	0.23	0.266	2.241

- Cobalt addition decreased Ni/Li exchange noticeably

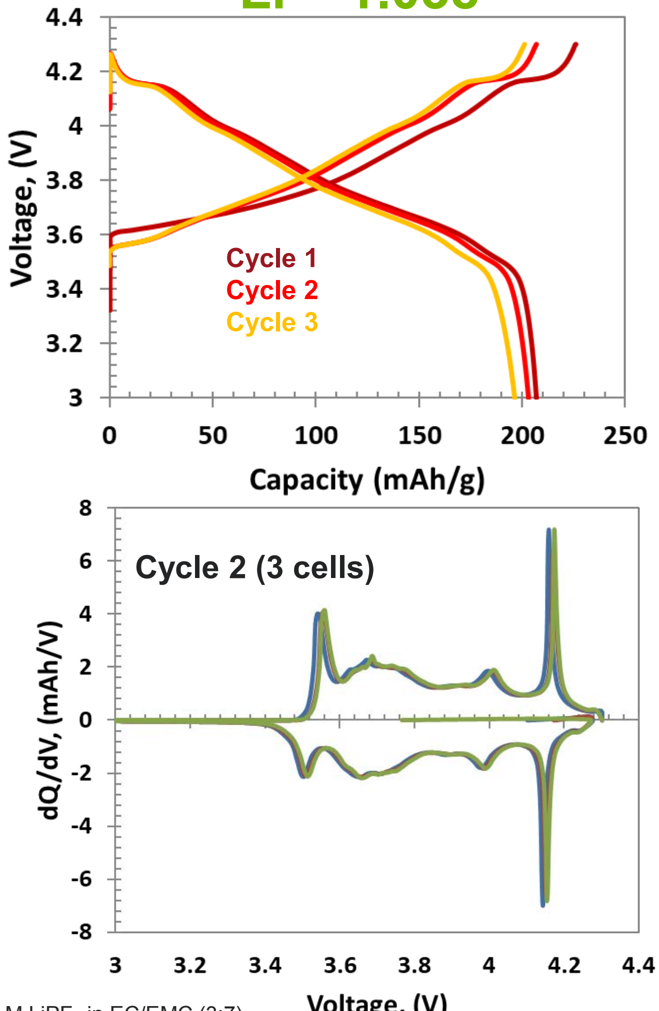
TECHNICAL ACCOMPLISHMENTS

Electrochemical Performance of $LiNi_{0.90}Co_{0.10}O_2$

725°C
Li = 1.053



775°C
Li = 1.038

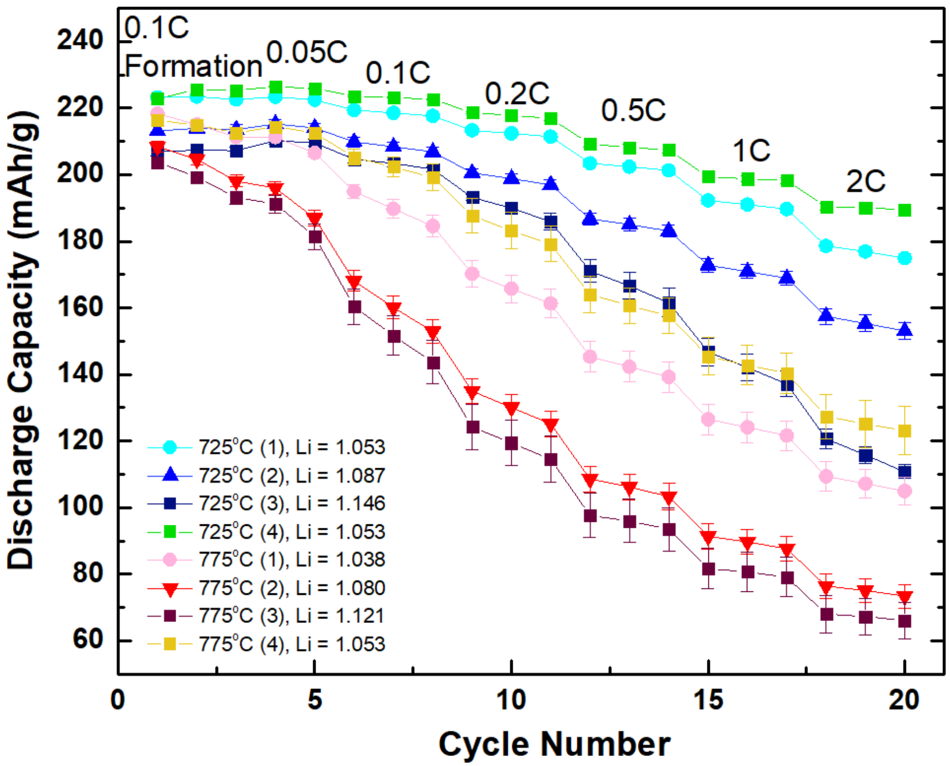


- More than 200 mAh/g capacity at 0.1C rate, when cycled between 3.0 – 4.3 V
- Cathode calcined at higher temperature exhibits greater capacity fade

Electrolyte: 1.2 M $LiPF_6$ in EC/EMC (3:7)
Potential Window: 3.0 - 4.3 V @30°C

TECHNICAL ACCOMPLISHMENTS

Electrochemical Rate Performance of $LiNi_{0.90}Co_{0.10}O_2$



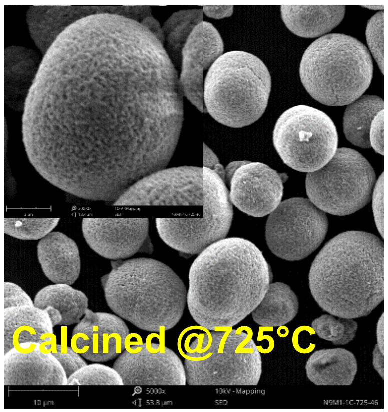
- Superior performance of cathode calcined at 725°C with lower lithium content

Sample	1st Cycle Efficiency (%)	1st Discharge (mAh/g)
725°C (1) Li = 1.053	96.2	223.2
725°C (2) Li = 1.087	94.4	213.2
725°C (3) Li = 1.146	93.4	206.9
725°C (4) Li = 1.053	95.7	222.8
775°C (1) Li = 1.038	94.0	218.4
775°C (2) Li = 1.080	91.9	208.4
775°C (3) Li = 1.121	91.3	203.8
775°C (4) Li = 1.053	94.3	216.3

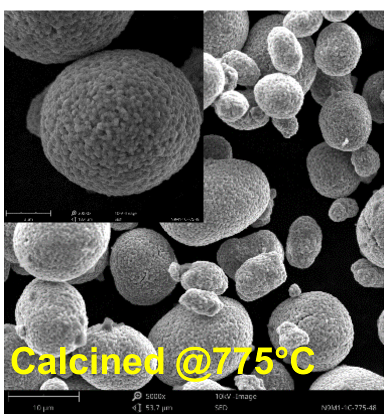
TECHNICAL ACCOMPLISHMENTS

Synthesis of $LiNi_{0.90}Mn_{0.10}O_2$

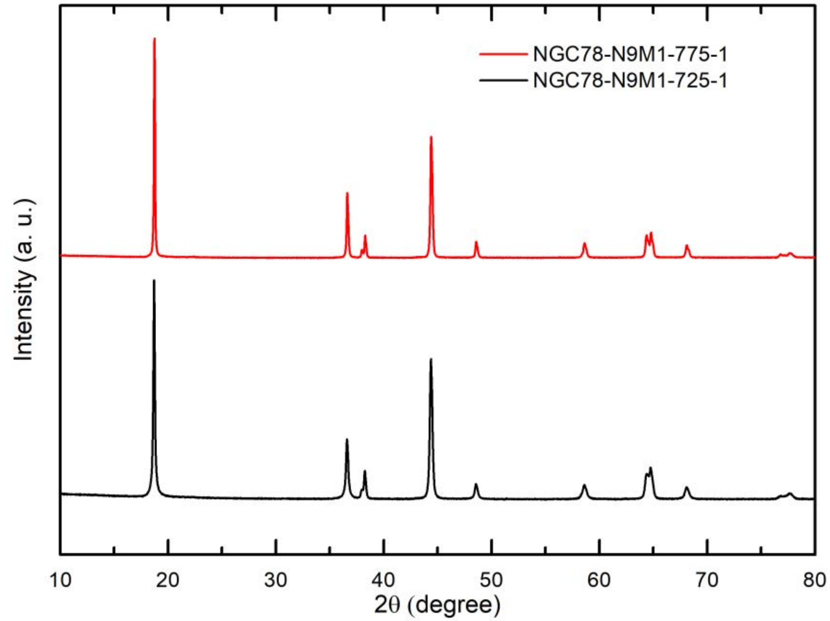
- Calcination optimization was carried out to adjust the Li ratio and to determine the optimal calcination temperature



Tap Density = 2.55 g/mL



Tap Density = 2.14 g/mL



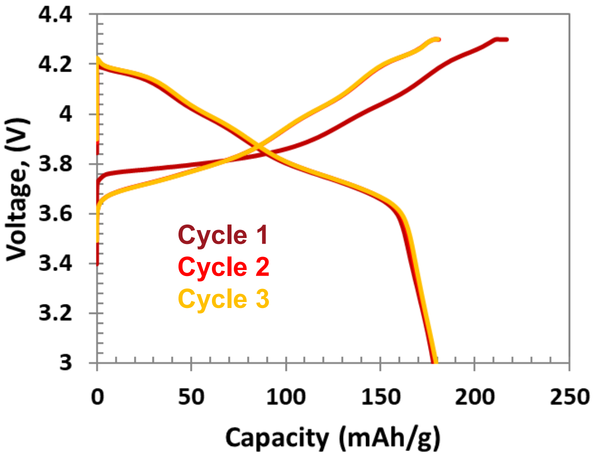
Sample	a (Å)	c (Å)	Ni/Li (%)	Crystallite size (μm)	Rw
NGC78-725-1	2.876	14.206	6.91	0.053	2.262
NGC78-775-1	2.877	14.217	3.71	0.145	2.185

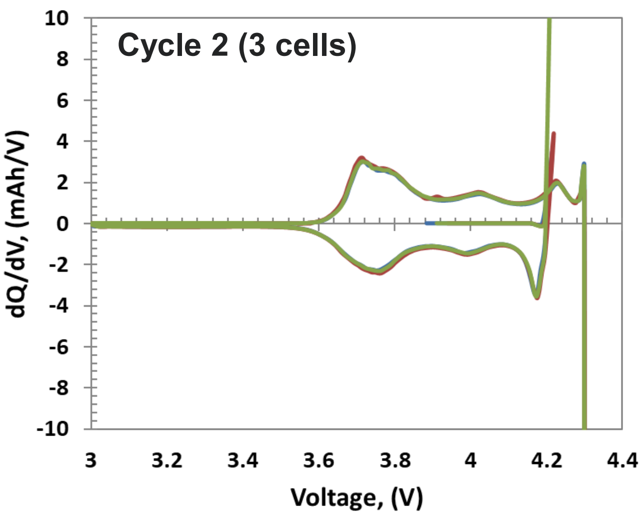
- Manganese increased Li/Ni exchange

TECHNICAL ACCOMPLISHMENTS

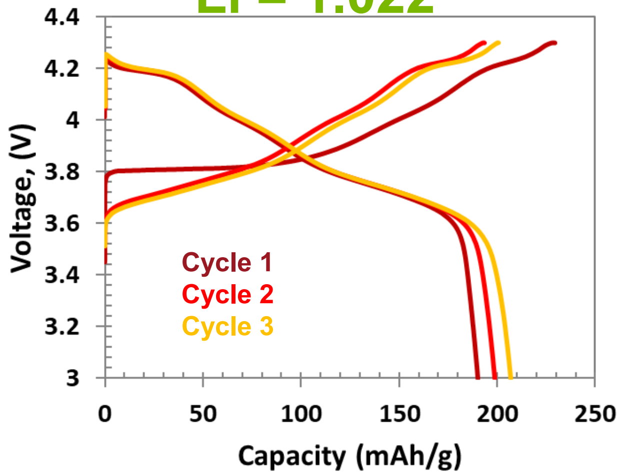
Electrochemical Performance of $LiNi_{0.90}Mn_{0.10}O_2$

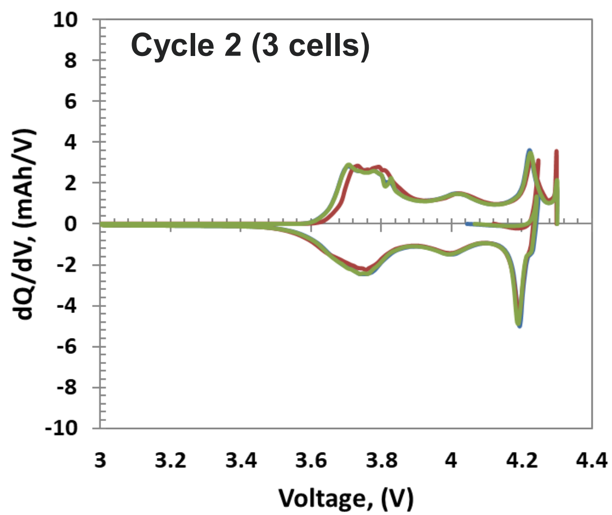
725°C
Li = 1.038





775°C
Li = 1.022



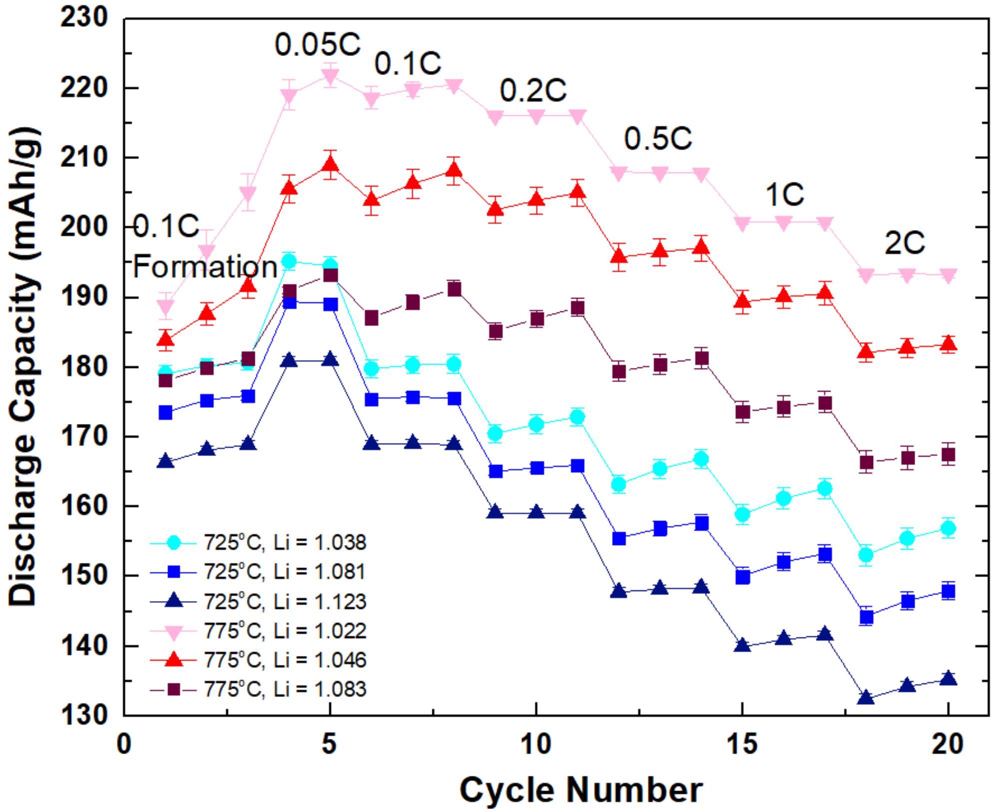


- Lower calcination temperatures displayed lower discharge capacities with a relatively stable cycling performance
- This composition requires higher calcination temperatures to exploit its intrinsic e-chem properties

Electrolyte: 1.2 M $LiPF_6$ in EC/EMC (3:7)
Potential Window: 3.0 - 4.3 V @30°C

TECHNICAL ACCOMPLISHMENTS

Electrochemical Rate Performance of $LiNi_{0.90}Mn_{0.10}O_2$

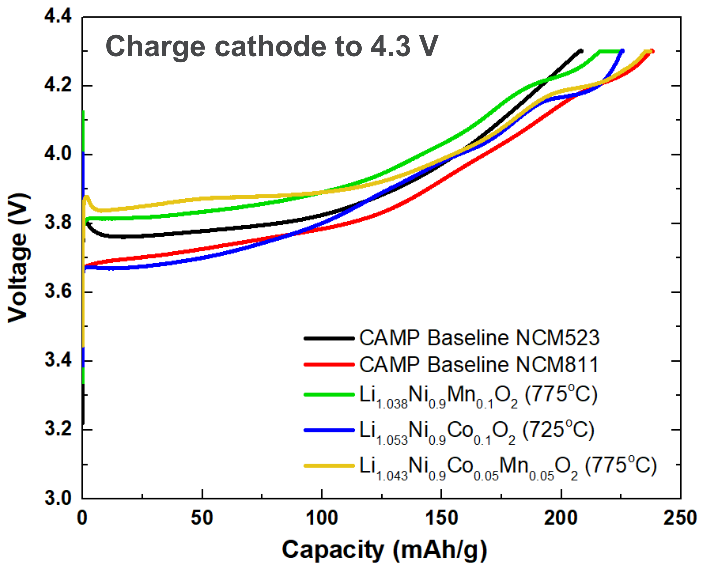


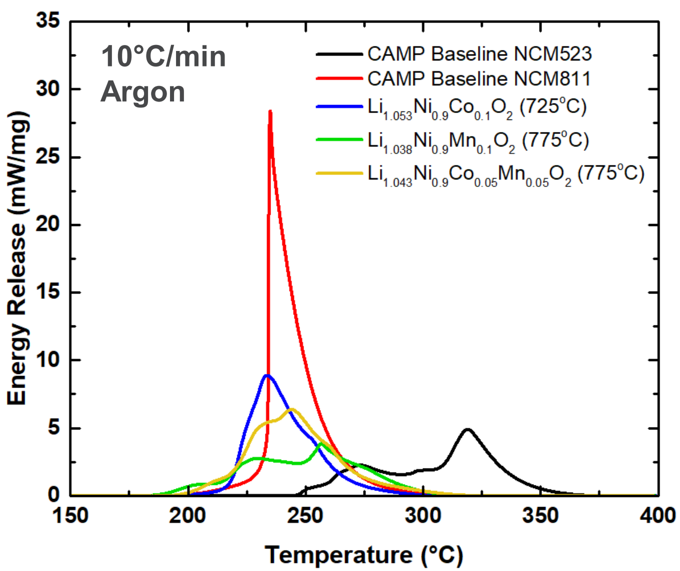
Sample	1st Cycle Efficiency (%)	1st Discharge (mAh/g)
725°C Li = 1.038	82.2	179.1
725°C Li = 1.081	81.3	173.6
725°C Li = 1.123	80.2	166.4
775°C Li = 1.022	82.5	188.8
775°C Li = 1.046	82.3	183.9
775°C Li = 1.083	82.2	178.1

- Further calcination optimization is considered at slightly elevated temperatures (e.g.; 800 and/or 825°C) to improve first cycle reversibility

TECHNICAL ACCOMPLISHMENTS

Preliminary Differential Scanning Calorimetry (DSC) of Ni-Rich Cathodes





- Investigate the effects of Co and Mn on the thermal stability of Ni-rich cathodes
- Onset of main peaks for 90% Ni-containing cathodes occurs at a lower temperature than NCM811 as expected
- DSC will be repeated once optimized calcination conditions are determined for each composition

Sample	Onset of Main Peak (°C)	Total Area, Heat Release (J/g)
NCM523	304(2)	1818(107)
NCM811	234(3)	2030(73)
$Li_{1.053}Ni_{0.9}Co_{0.1}O_2$	217(1)	1977(87)
$Li_{1.038}Ni_{0.9}Mn_{0.1}O_2$	209(6)	2138(125)
$Li_{1.043}Ni_{0.9}Co_{0.05}Mn_{0.05}O_2$	213(5)	2075(82)

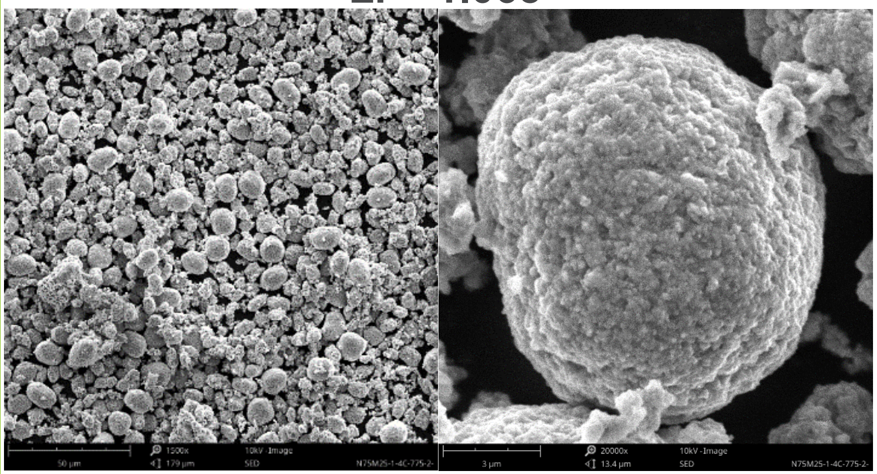
*Onset and Total Area calculated from Netzsch Proteus Analysis software and averaged for each data set. All errors shown as 2*StdDev. Instrument: Netzsch STA 449 F3 Jupiter DSC.*

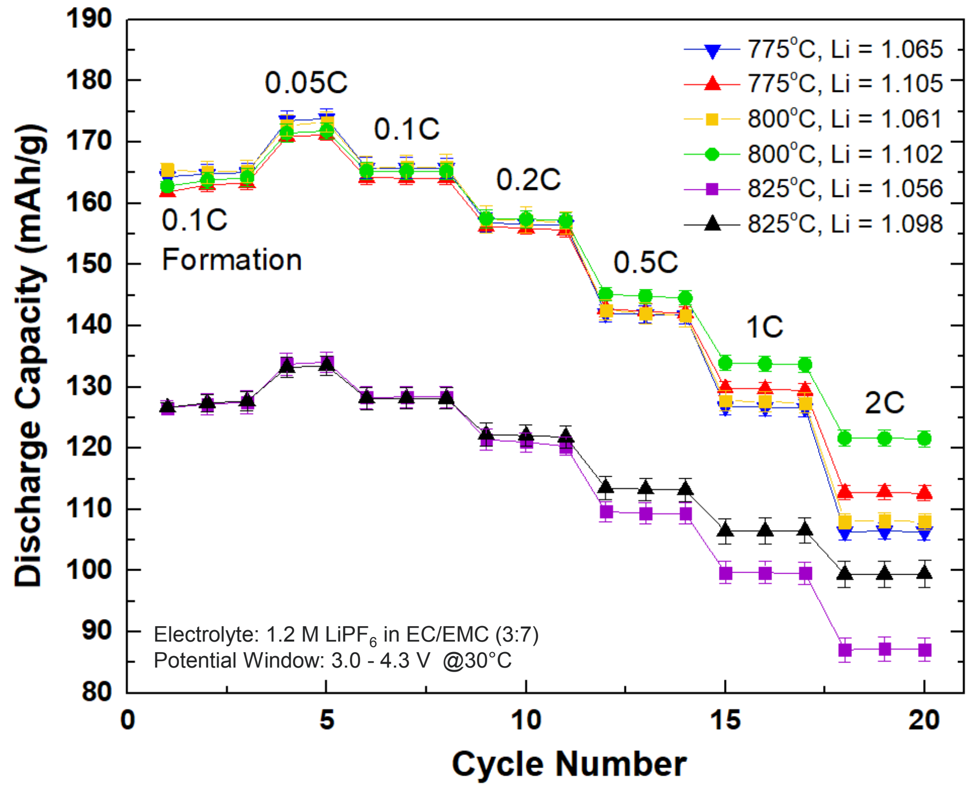
TECHNICAL ACCOMPLISHMENTS

Synthesis of $LiNi_{0.75}Mn_{0.25}O_2$

- Synthesis of $LiNi_{0.75}Mn_{0.25}O_2$ by using a 4L **C**ontinuously **S**tirred **T**ank **R**eactor (**CSTR**)

775°C
Li = 1.065





- Further co-precipitation (+calcination) optimization is required to improve the morphology of the particles.
- Calcination temperatures higher than 800°C, resulted in ~45 mAh/g lower capacity values then that of with lower calcination temperatures

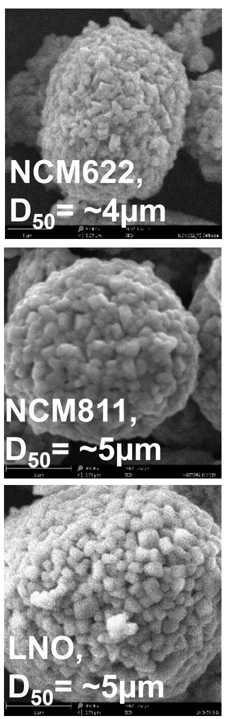
This material was requested when the TVR was undergoing routine maintenance and CSTR was used for synthesis. We delivered the material to Fulya Dogan Key (ANL, CSE) for solid state NMR studies.

TECHNICAL ACCOMPLISHMENTS

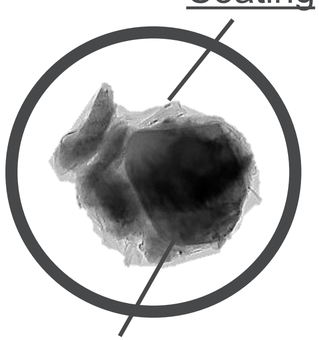
Small NCM Particles Synthesized in TVR

- Advanced particle coatings typically require smaller NMC particles for conformal and efficient coating
- Good performing, small and spherical NCM secondary particles below and/or around 5 µm are not commercially available
- Upon request; various small NMC particles with a D50 value of ≤ 5µm were generated using TVR to enable an advanced coating technology which is compatible with particle sizes ranging between 100nm up to 8 µm

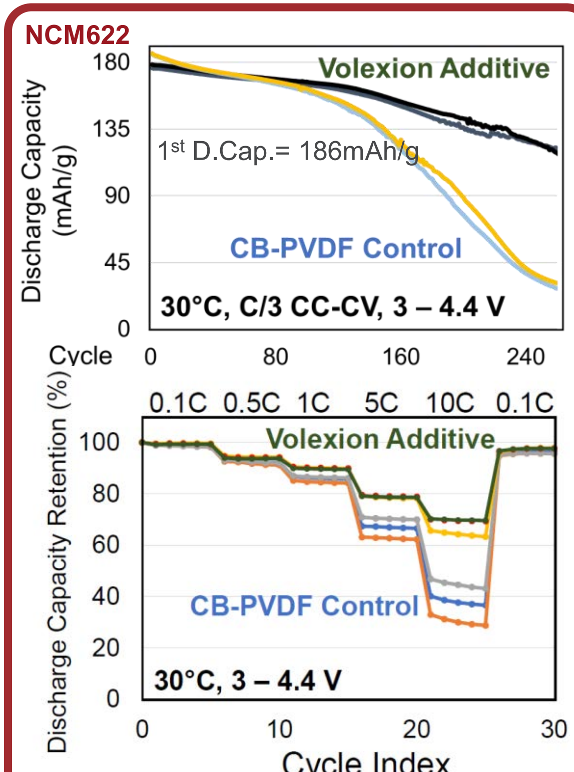
MERF-made

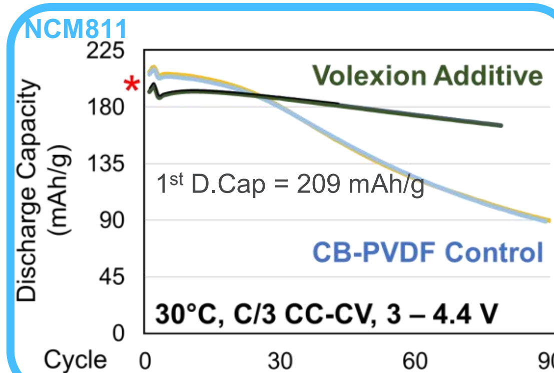


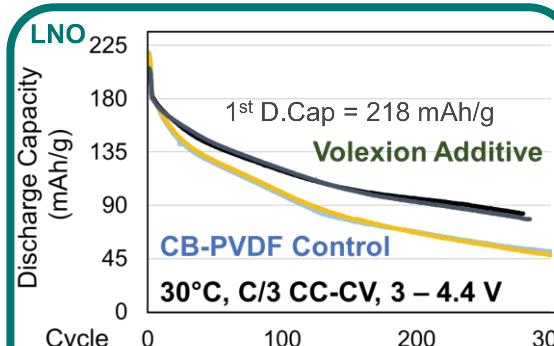
Graphene Coating by Volexion



volexion



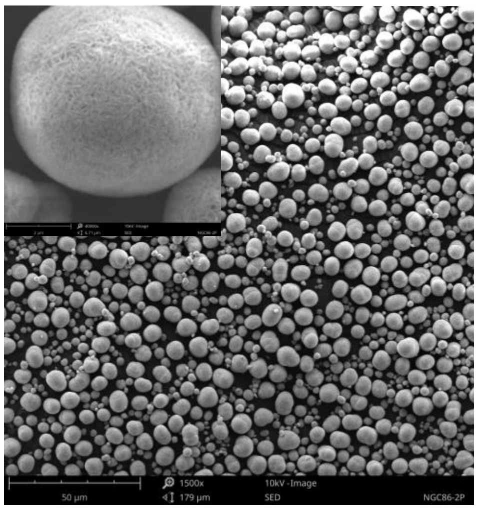




TECHNICAL ACCOMPLISHMENTS

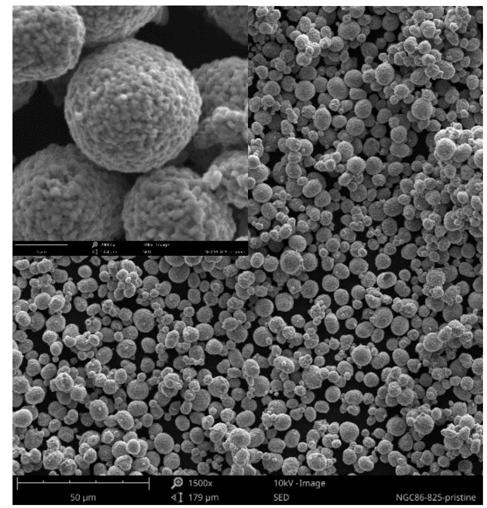
Scalability Evaluation of Taylor Vortex Reactor – from 1L to 10L

- Small, dense, spherical, secondary NCM particles between 5 – 8 µm are not commercially available
- $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ hydroxide precursor was produced at ~2.0kg scale using 10L TVR



$Ni_{0.794}Co_{0.104}Mn_{0.102}(OH)_2$
D_{50} = **6.3 µm**
Tap density = 1.78 g/cc

Calcination
825°C, O_2
Deagglomeration



$Li_{1.039}Ni_{0.793}Co_{0.105}Mn_{0.103}O_2$
D_{50} = 7.4 µm
Tap density = 1.93 g/cc

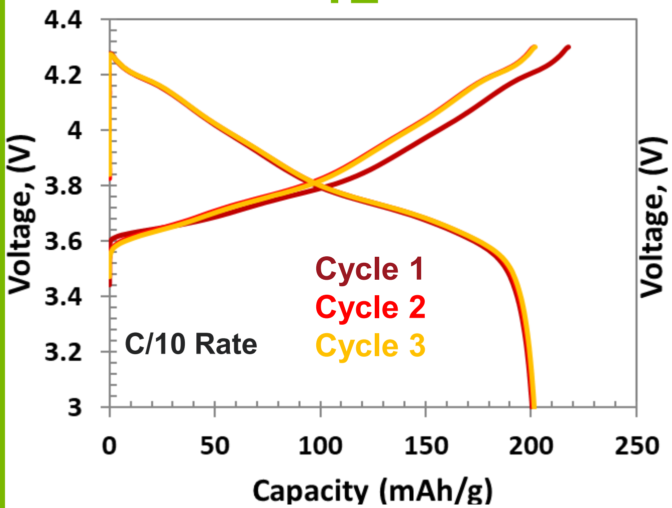
- Target specs (D_{50} = 5-8 µm) were achieved at the very first scale-up run, using 10L TVR

In support for BAT164 (Jianlin Li, ORNL)
Materials provided to Volexion & Blue Current

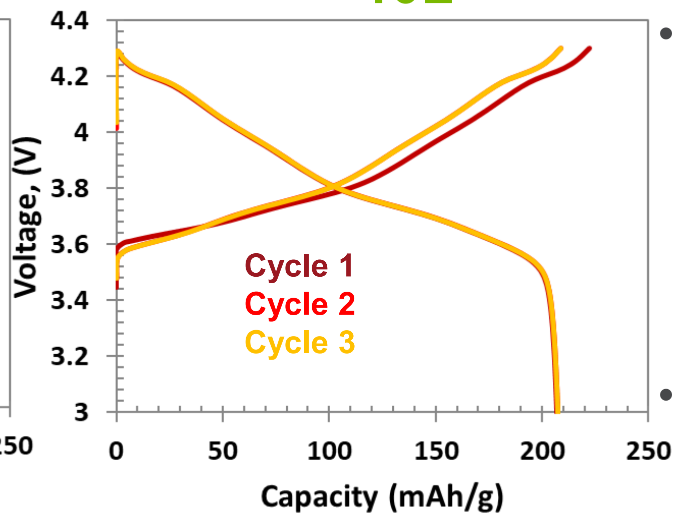
TECHNICAL ACCOMPLISHMENTS

Electrochemical Performance Comparison of TVR Scalability Experiments

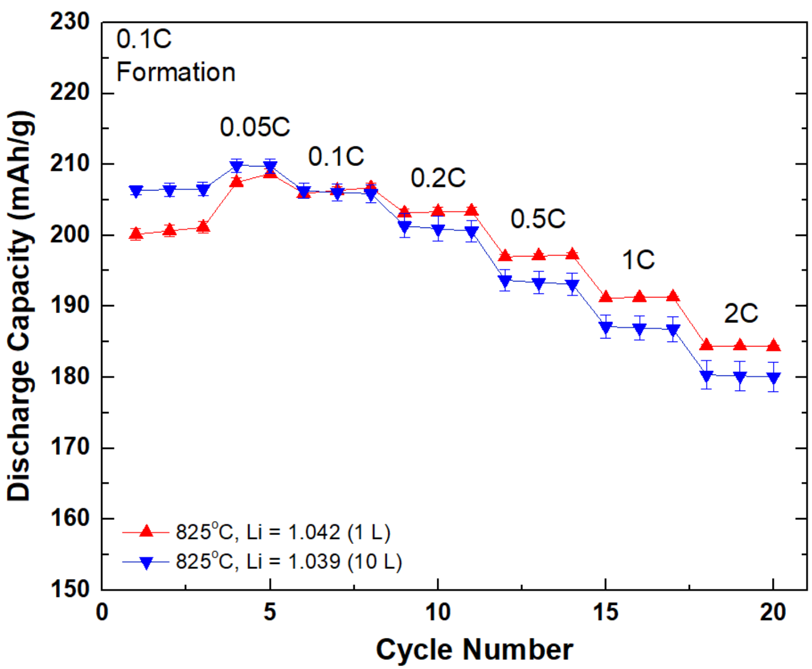
1L



10L



- Similar voltage profiles were observed; with the scaled up material having slightly higher initial discharge capacity
- Large scale calcination is on-going



Sample	1st Cycle Efficiency (%)	1st Discharge (mAh/g)
825°C Li = 1.042 (1 L)	92.1	200.1
825°C Li = 1.039 (10 L)	93.1	206.4

Electrolyte: 1.2 M $LiPF_6$ in EC/EMC (3:7)
Potential Window: 3.0 - 4.3 V @30°C

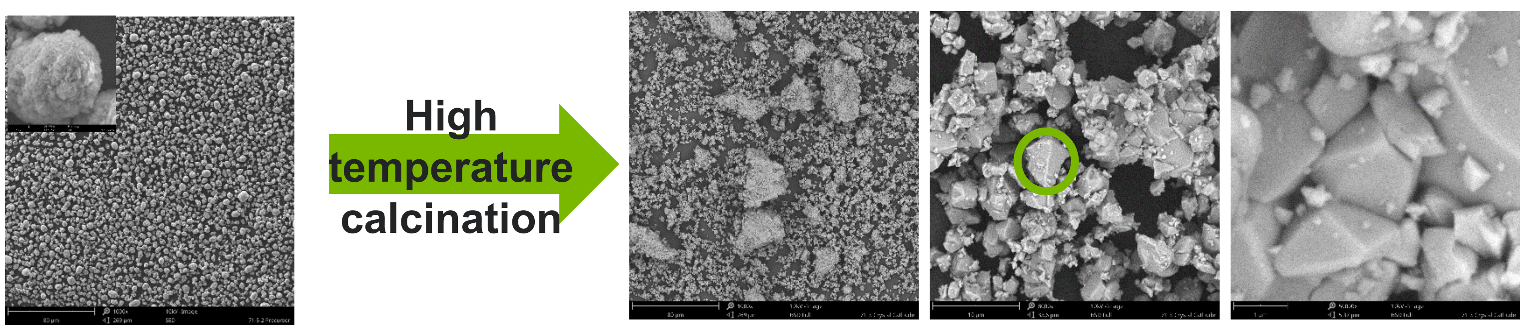
TECHNICAL ACCOMPLISHMENTS

Single Crystal Preliminary Studies

- A growing interest on using micron size single crystals as cathode active materials
  - These particles reduce surface area and thereby reduce surface reactions
    - Increased cycle life
    - Improved safety characteristics
    - ***Potential for increasing voltage window***

- Generating <5 µm dense particles (by TVR) and further applying long term calcinations to enlarge/fuse the primary particles to single crystal
- Preliminary studies used $LiNiO_2$ to show the ability of making single crystals;

Precursor **850°C**



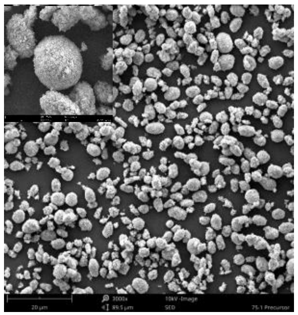
- Some particles were grown as big as 6 µm with strong agglomeration
- Optimization is required for controlling the Li amount and de-agglomerating the particles

TECHNICAL ACCOMPLISHMENTS

Single Crystal NCM622 Particles - Preliminary

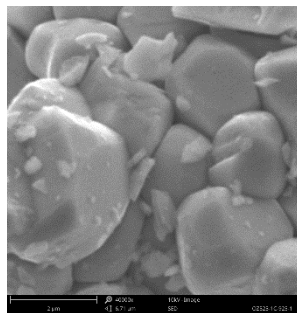
- Denser particles were prepared at high calcination temperatures using NMC622 hydroxide precursor with ~3.5 µm particle sizes made by TVR

Precursor

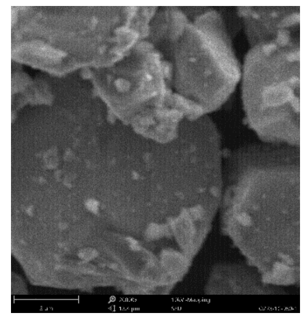


High temperature calcination

925°C



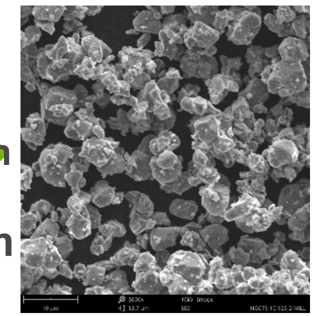
950°C

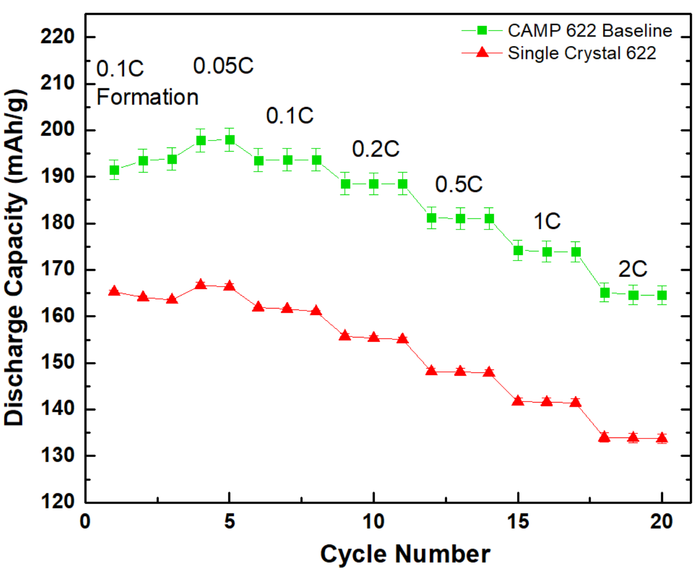


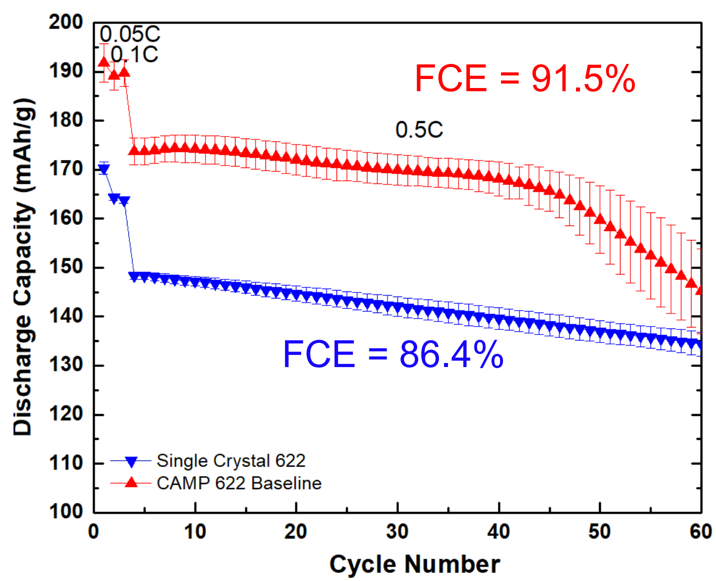
De-agglomeration

D_{50} = 7.40 µm

925°C







Further optimization is required to achieve similar/close electrochemical performance with the commercial **baseline NCM622 secondary particles**

Response To Previous Year Reviewers' Comments

- There were no comments or questions from last year

COLLABORATIONS

- Deep-Dive into Next-Generation Cathode Materials (2A): Realizing the Potential of Layered Transition-Metal Oxide (BAT375)
  - Gabriel Veith (ORNL) → ~350 g of hydroxide precursors for in-situ neutron studies: $Ni(OH)_2$, $Ni_{0.90}Co_{0.05}Mn_{0.05}(OH)_2$, $Ni_{0.90}Co_{0.10}(OH)_2$, $Ni_{0.90}Mn_{0.10}(OH)_2$
  - Christopher Johnson (ANL) → ~104 g of $Ni(OH)_2$ for ion exchange study
  - Fulya Dogan Key (ANL) → $LiNi_{0.75}Mn_{0.25}O_2$ and $LiNiO_2$: Solid state NMR studies
  - Bryant Polzin (ANL) → $LiNiO_2$: for full cell evaluation (comparison of preliminary and semi-optimized LNO made by MERF and commercial companies)
- Thick, Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing (BAT164)
  - Jianlin Li (ORNL) →Scale up of 1kg small NCM811 @ 10L TVR
- Chain Reaction Innovations Program (Volexion)
  - Jung Woo Seo → Small NCM622, NCM811, LNO for proprietary graphene coating
- Blue Current
  - Kevin Wujcik → 50 g of each: small NCM622, NCM811 for the development of All-Solid-State batteries

ACTIVITIES FOR NEXT FISCAL YEAR

- Explore the effects of adding dopants during synthesis of Ni-rich materials produced this fiscal year
  - Differential Scanning Calorimetry (DSC) of pristine and doped materials
  - In-situ XAS of pristine and doped materials
- Optimization of the processes to create higher quality single crystal cathode materials
- Continue supporting battery research community by providing and making available advanced cathode materials
  - ≤ 5 µm small NCM particles (e.g.; NCM622, NCM811, NCM900505 and etc.)
  - 1-10 µm single crystal NCM particles
  - Commercially unavailable cathode compositions (e.g.; Ni-rich cathodes)
  - Commercially unavailable cathode morphologies (e.g.; good performing small particles (D_{50}= 4-8 µm), single crystals)
- Scale up and process optimization of promising new cathode materials
  - Suggestions are welcome for scaling up newly invented, promising battery materials

SUMMARY

- **In support of "Deep-Dive into Next-Generation Cathode Materials"**
  - Synthesized at 1L TVR (Hundreds of grams each)
    - $Ni(OH)_2$, $Ni_{0.90}Co_{0.05}Mn_{0.05}(OH)_2$, $Ni_{0.90}Co_{0.10}(OH)_2$, $Ni_{0.90}Mn_{0.10}(OH)_2$
    - ~500 grams of hydroxide precursor were delivered to the participants
    - Respective cathodes were evaluated at half-coin cell format
    - Initial DSC studies were conducted on cathode materials
  - Synthesized at 4L CSTR (~600g): $Ni_{0.75}Mn_{0.25}(OH)_2$
- **Small NCM Particles (D_{50} = 4~8μm) Synthesized in TVR**
  - Multiple 100s g $LiNiO_2$
  - >100 g $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$
  - ~2.0 kg $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$
- **Single Crystal NCM Particles (D_{50} = 1~6μm)**
  - $LiNiO_2$
  - $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$
  - $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$
  - $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$
- **Scalability Evaluation of Taylor Vortex Reactor**
  - 10L TVR run: ~2.0 kg of $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$
- TVR is the preferred platform for **rapidly** making advanced cathode materials with desired morphologies and compositions

ACKNOWLEDGEMENTS AND CONTRIBUTORS

- Continuous support from Peter Faguy and David Howell of the U.S. Department of Energy's Office of Vehicle Technologies is greatly appreciated.
- Contributors
  - Jessica Durham
  - Albert Lipson
  - Shankar Aryal
  - Kris Pupek
  - Donghao Liu
  - Nick Sovronec
  - Brad Ross
  - Michael LeResche
  - Bryant Polzin
  - Alison Dunlop
  - Steve Trask
  - Gerald Jeka
  - Jessica Scott
  - Guy Reynolds

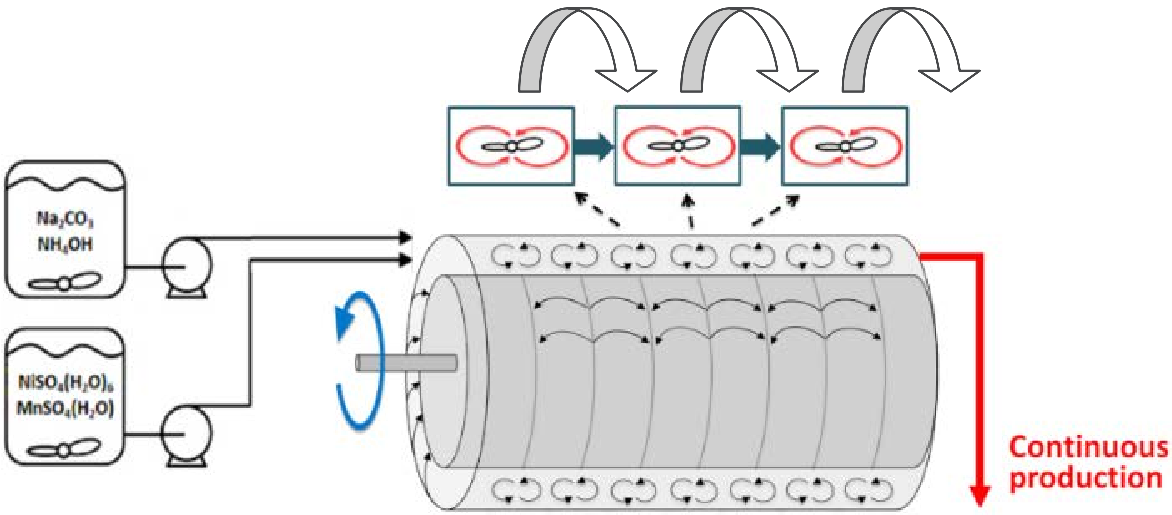
Samples request and further information:

www.anl.gov/merf

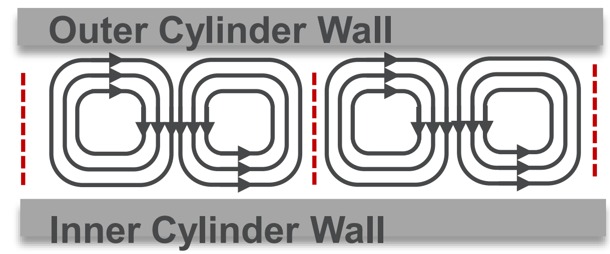
TECHNICAL BACKUP SLIDES

TECHNICAL BACKUP

Taylor Vortex Reactor



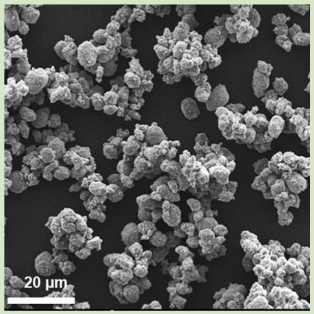
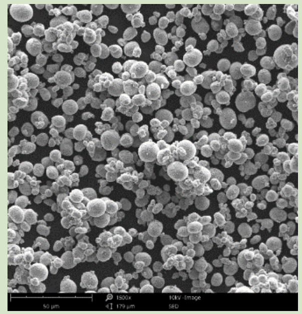
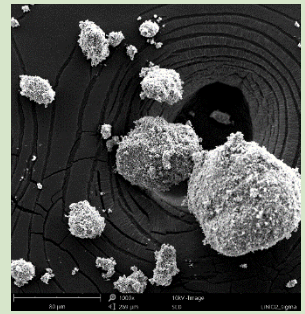
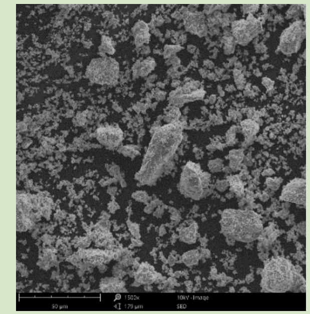
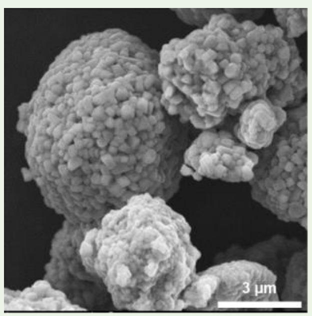
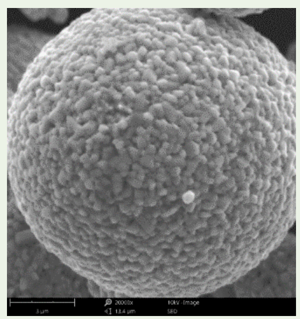
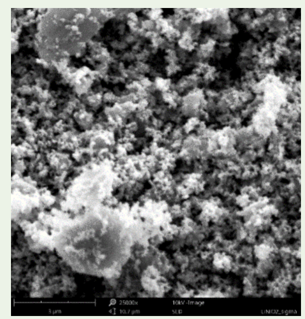
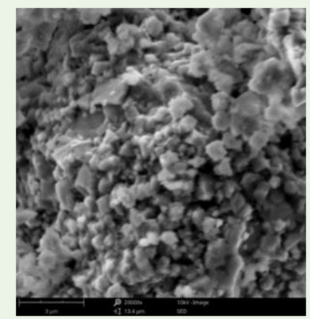
Each unitary vortex cell : enabling micro-mixing



<u>Homogeneous intense micro-mixing zone: faster reaction kinetics</u>

- High mass and heat transfer: high degree of uniform supersaturation
- Self particle size control: high fluid shear → breakage and re-dispersion
- No dead-zone : improvement of purity, morphology, particle size & distribution, degree of crystallinity
- Key variables affecting fluid motion are **hydrodynamic intensity (rotation speed)** and **dimensions (gap size)** of Taylor vortex

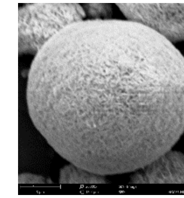
$LiNiO_2$ from Different Vendors vs ANL-made

#71_MERF-preliminary	#85_MERF-representative	#83_Vendor A	#87_Vendor B
			
			

Sample #	ICP	Tap density	PSA	1st Discharge Capacity
#71_MERF-preliminary	$Li_{1.06}NiO_2$	1.71 g/cc	4.2 / 9.2 / 19.2 μm (Mean =10μm)	231 mAh/g
#85_MERF-representative	$Li_{1.00}NiO_2$	2.10 g/cc	6.52 / 12.06 / 22.15μm (Mean = 13.40 μm)	222 mAh/g
#83_Vendor A	$Li_{1.28}NiO_2$	0.85 g/cc	0.19 / 2.62 / 11.35μm (Mean= 4.36μm)	N/A
#87_Vendor B	$Li_{0.95}NiO_2$	2.32 g/cc	0.83 / 8.71 / 18.39 μm (Mean = 9.13 μm)	156 mAh/g

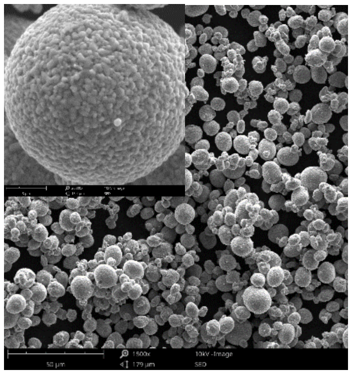
$LiNiO_2$ Calcination Optimization Studies

Former **Ni (OH)$_2$** precursor; 1.89g/cc

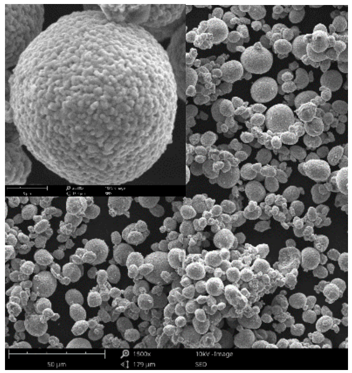


SEM – Cathode calcined at 725°C

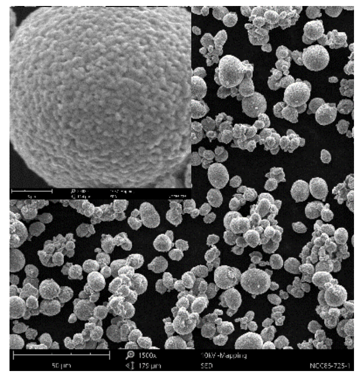
$Li_{1.004}NiO_2$



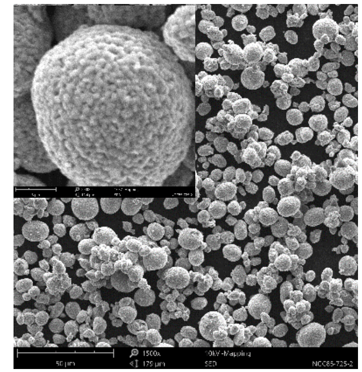
$Li_{1.031}NiO_2$



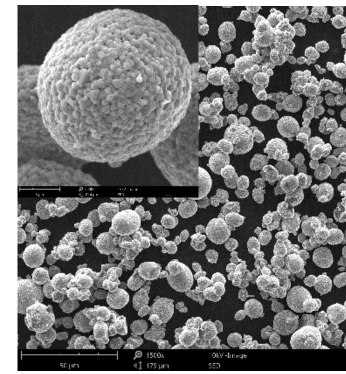
$Li_{1.063}NiO_2$



$Li_{1.110}NiO_2$

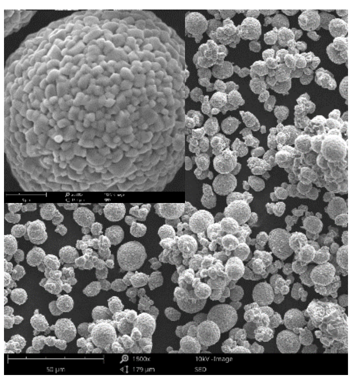


$Li_{1.137}NiO_2$

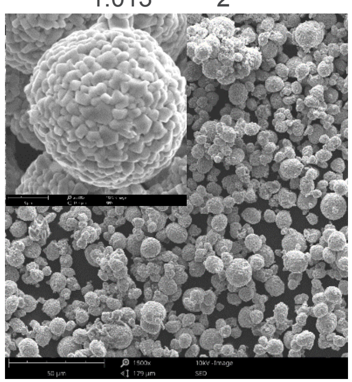


SEM – Cathode calcined at 775°C

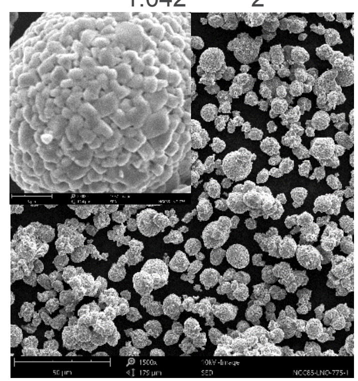
$Li_{1.000}NiO_2$



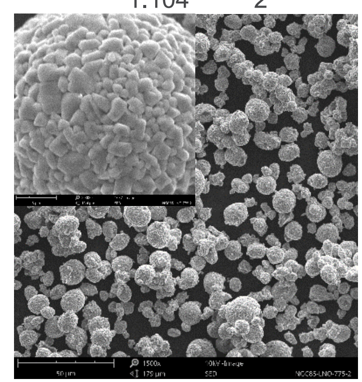
$Li_{1.013}NiO_2$



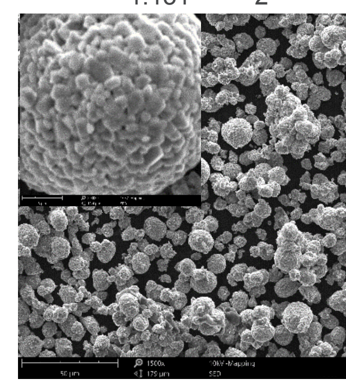
$Li_{1.042}NiO_2$



$Li_{1.104}NiO_2$



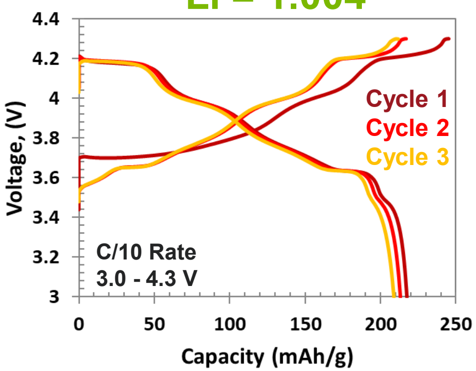
$Li_{1.131}NiO_2$

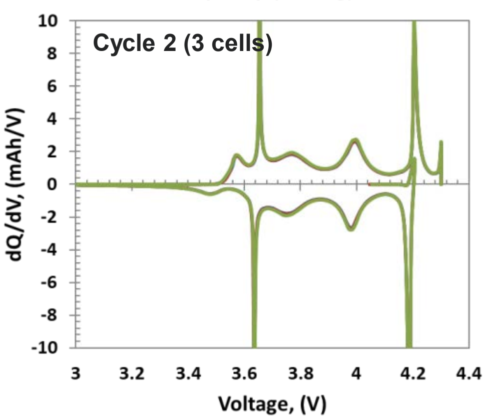


$LiNiO_2$

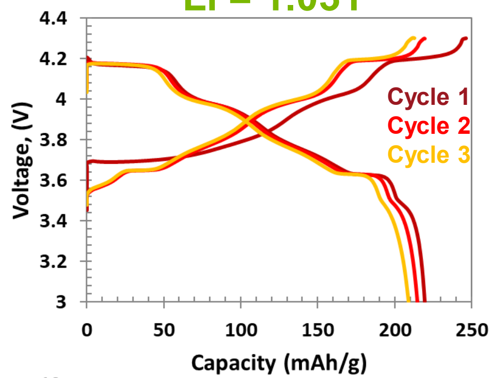
Electrochemistry – 725°C Formation Cycles

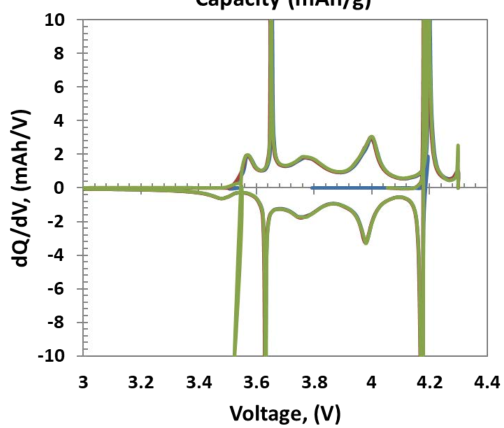
725°C
Li = 1.004



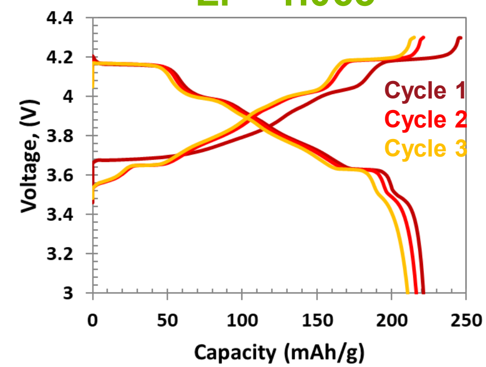


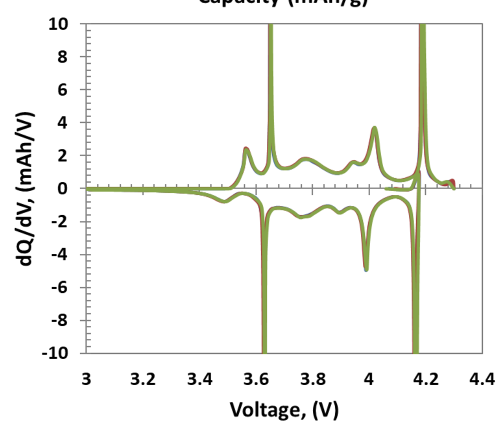
725°C
Li = 1.031





725°C
Li = 1.063

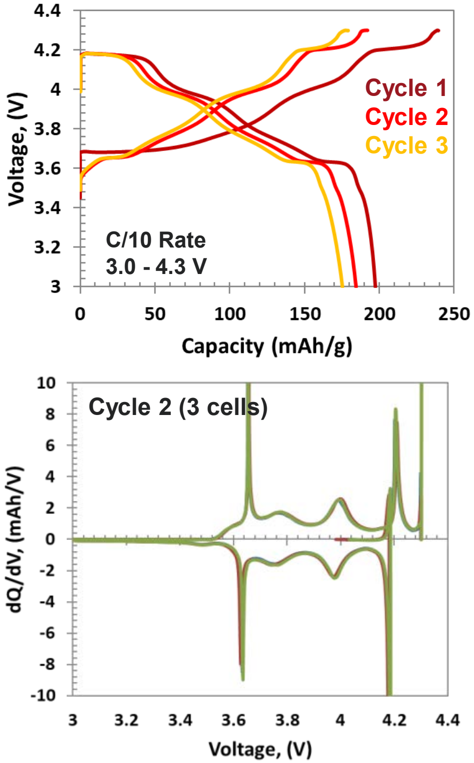




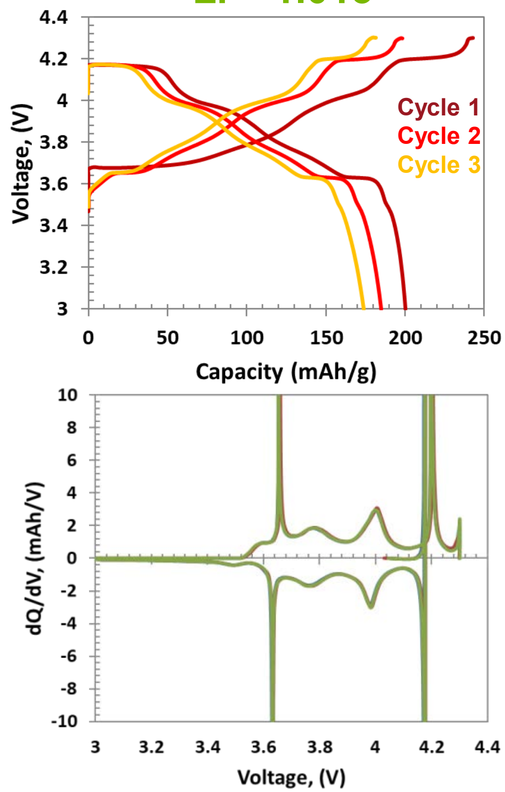
$LiNiO_2$

Electrochemistry – 775°C Formation Cycles

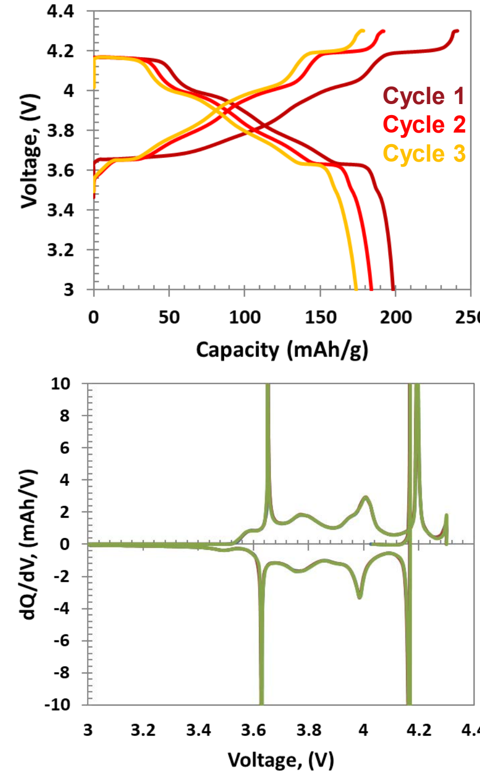
775°C
Li = 1.000



775°C
Li = 1.013

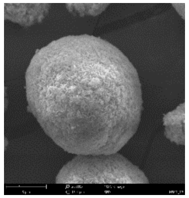


775°C
Li = 1.042



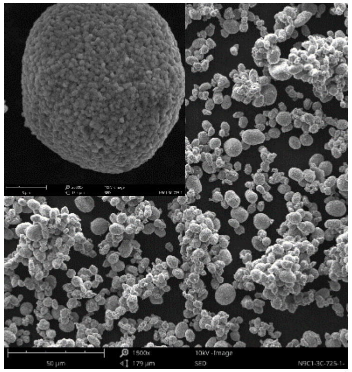
$LiNi_{0.9}Co_{0.1}O_2$ Calcination Optimization Studies

Former $\mathbf{Ni_{0.9}Co_{0.1}(OH)_2}$ precursor; 1.73g/cc

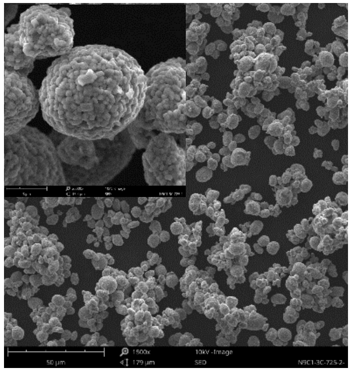


SEM – Cathode calcined at 725°C

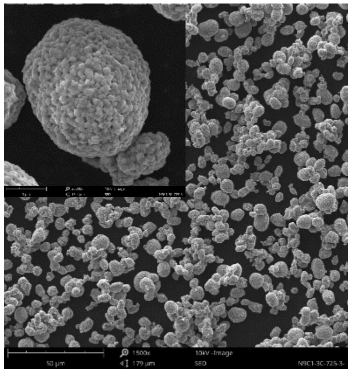
$Li_{1.053}Ni_{0.891}Co_{0.109}O_2$



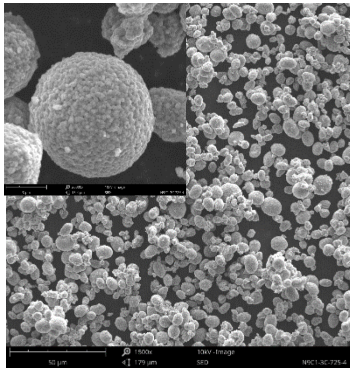
$Li_{1.087}Ni_{0.891}Co_{0.109}O_2$



$Li_{1.146}Ni_{0.891}Co_{0.109}O_2$

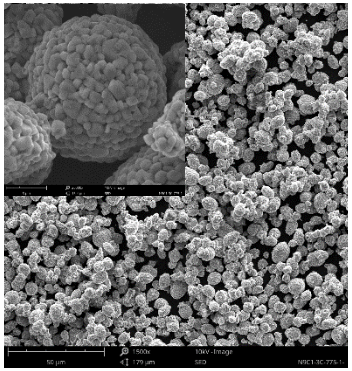


$Li_{1.053}Ni_{0.887}Co_{0.113}O_2$

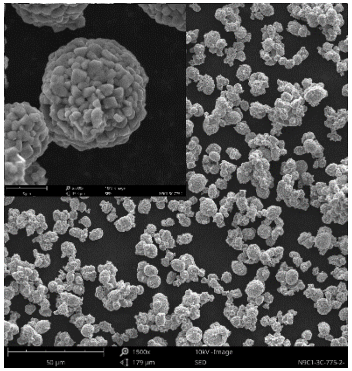


SEM – Cathode calcined at 775°C

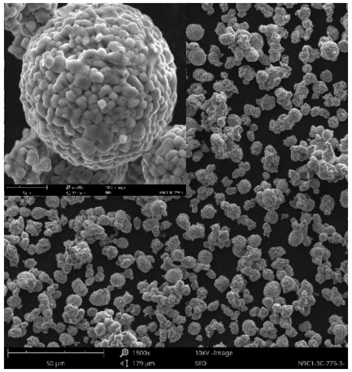
$Li_{1.038}Ni_{0.891}Co_{0.109}O_2$



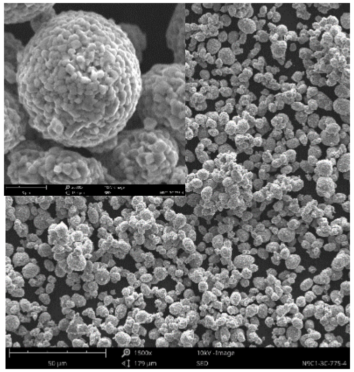
$Li_{1.080}Ni_{0.891}Co_{0.109}O_2$



$Li_{1.121}Ni_{0.891}Co_{0.109}O_2$

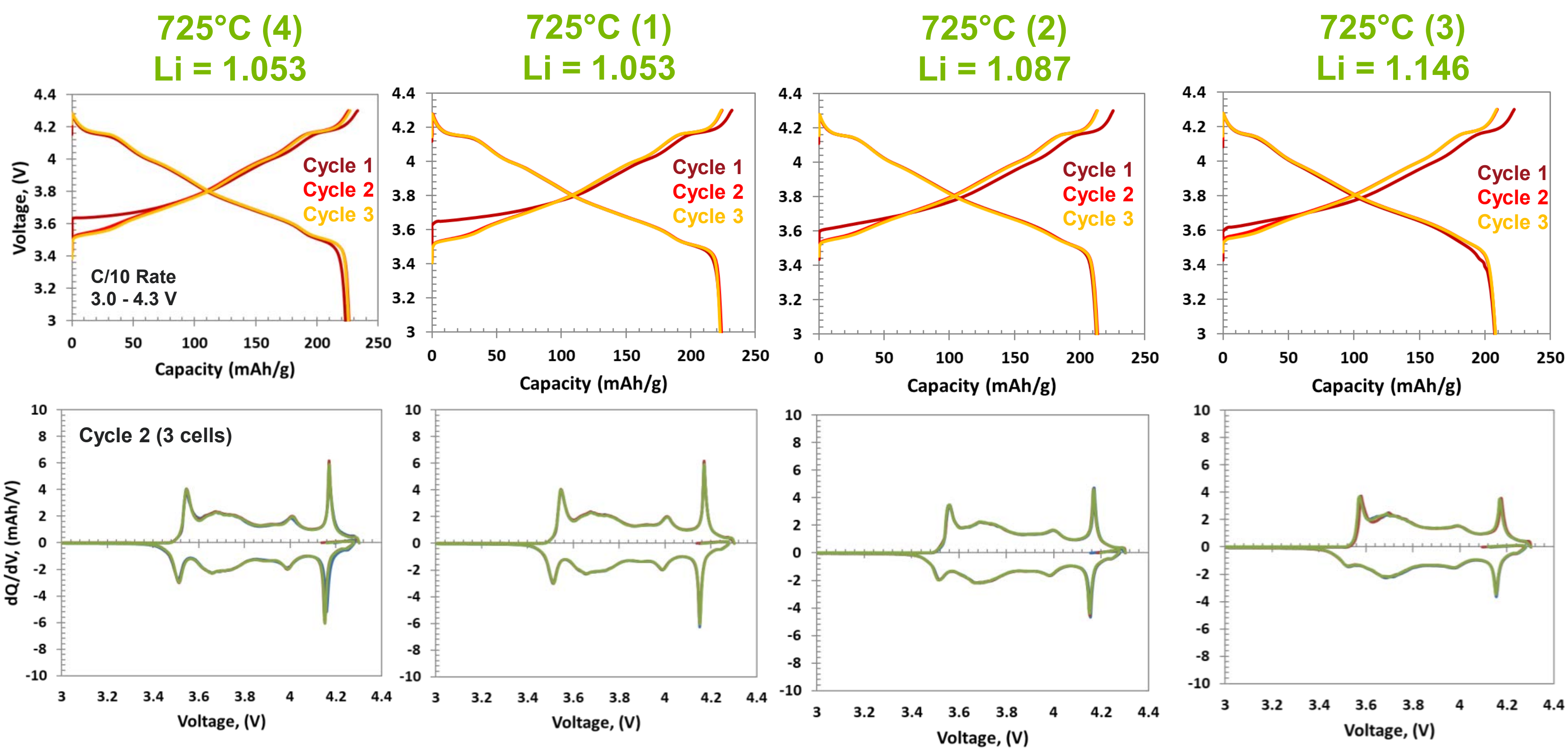


$Li_{1.053}Ni_{0.887}Co_{0.113}O_2$



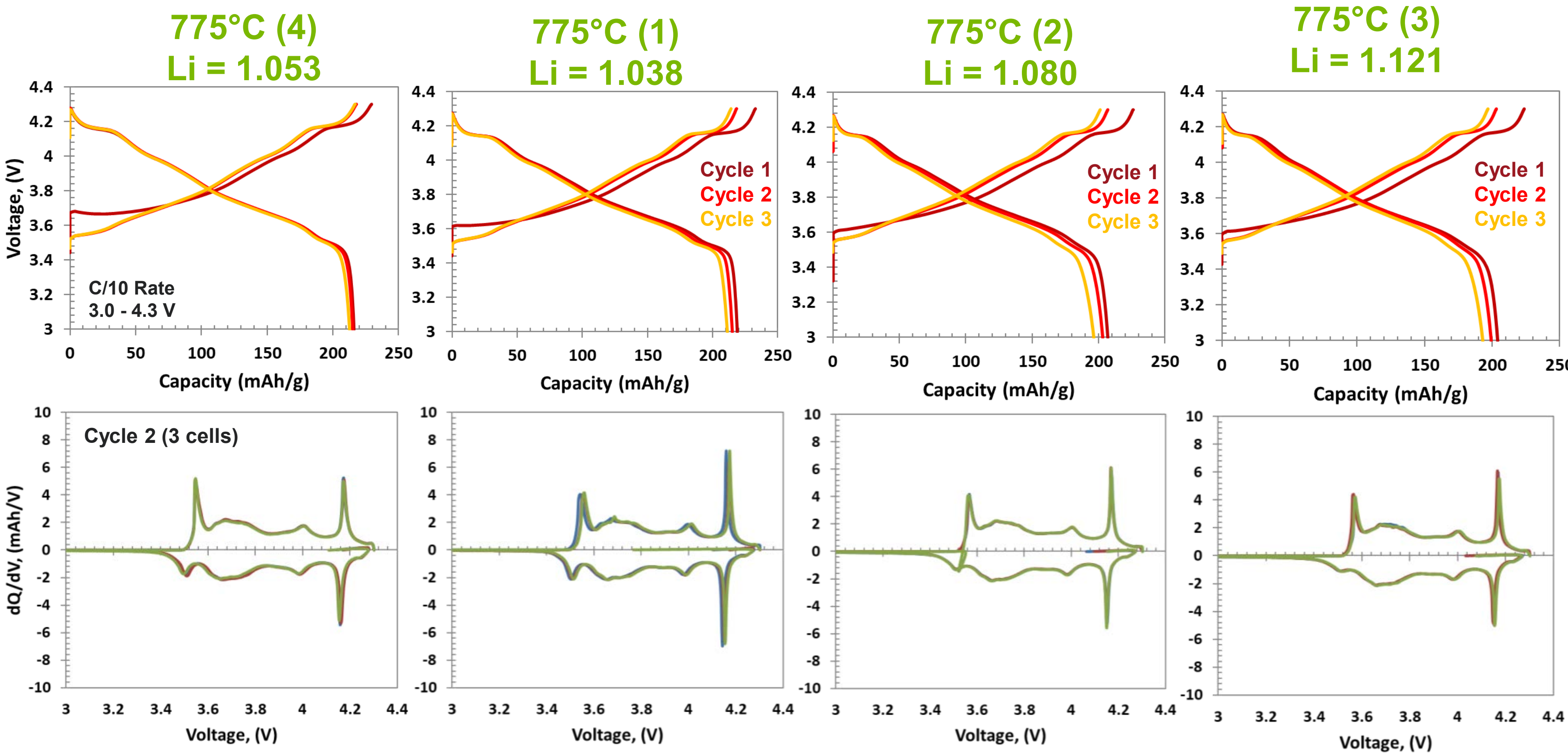
$LiNi_{0.9}Co_{0.1}O_2$

Electrochemistry – 725°C Formation Cycles



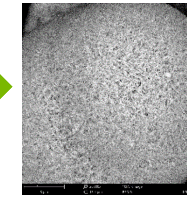
$LiNi_{0.9}Co_{0.1}O_2$

Electrochemistry – 775°C Formation Cycles



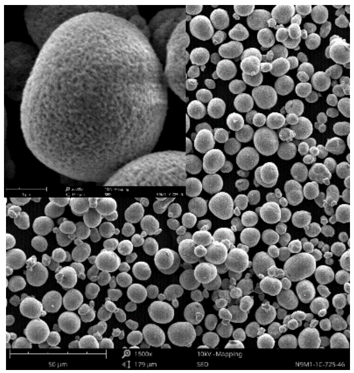
$LiNi_{0.9}Mn_{0.1}O_2$ Calcination Optimization Studies

Former $\mathbf{Ni_{0.9}Mn_{0.1}(OH)_2}$ precursor; 1.91g/cc

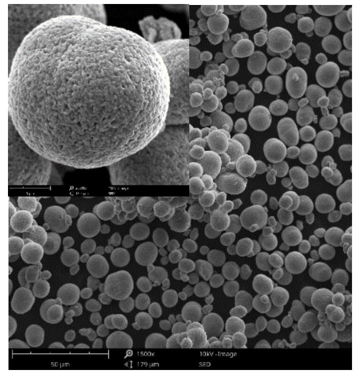


SEM – Cathode calcined at 725°C

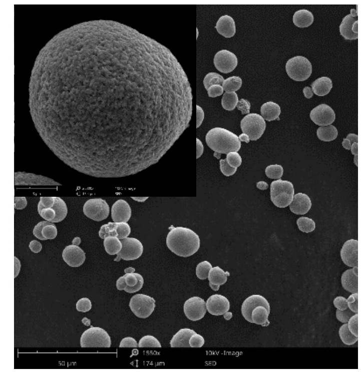
$Li_{1.038}Ni_{0.891}Mn_{0.109}O_2$



$Li_{1.081}Ni_{0.891}Mn_{0.109}O_2$

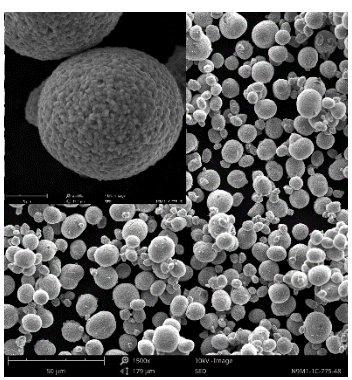


$Li_{1.123}Ni_{0.891}Mn_{0.109}O_2$

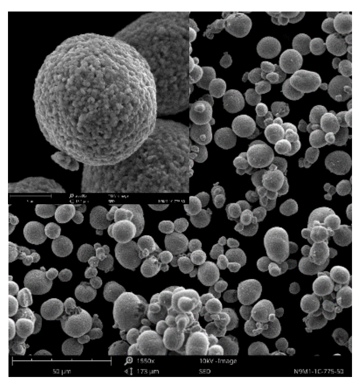


SEM – Cathode calcined at 775°C

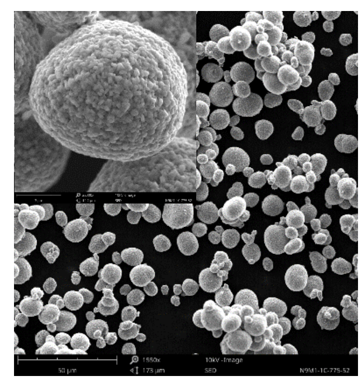
$Li_{1.022}Ni_{0.891}Mn_{0.109}O_2$



$Li_{1.046}Ni_{0.891}Mn_{0.109}O_2$



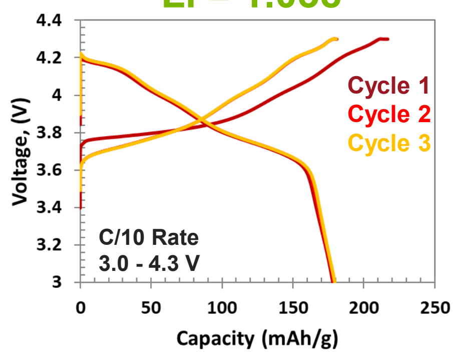
$Li_{1.083}Ni_{0.891}Mn_{0.109}O_2$

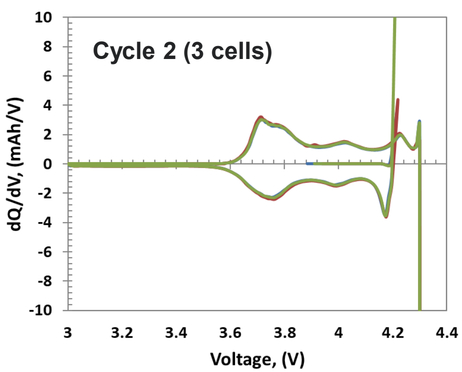


$LiNi_{0.9}Mn_{0.1}O_2$

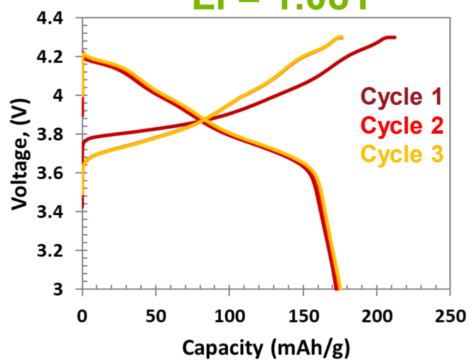
Electrochemistry – 725°C Formation Cycles

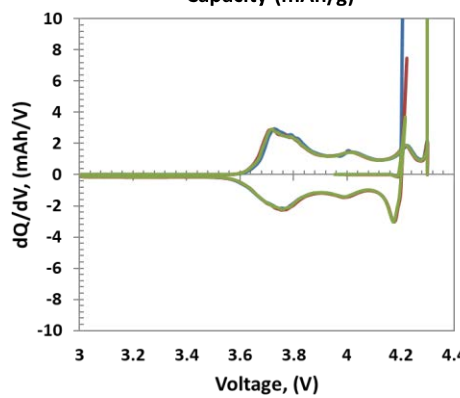
725°C
Li = 1.038



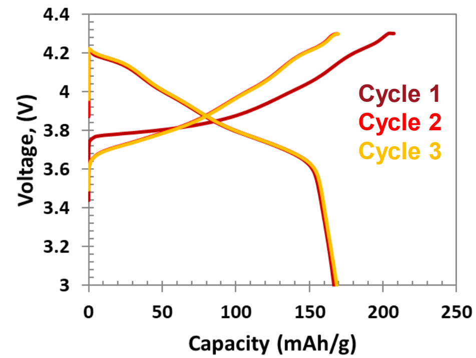


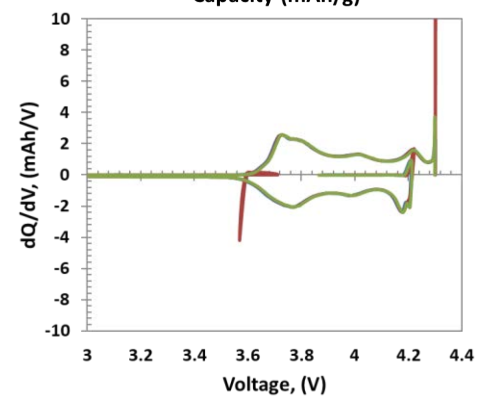
725°C
Li = 1.081





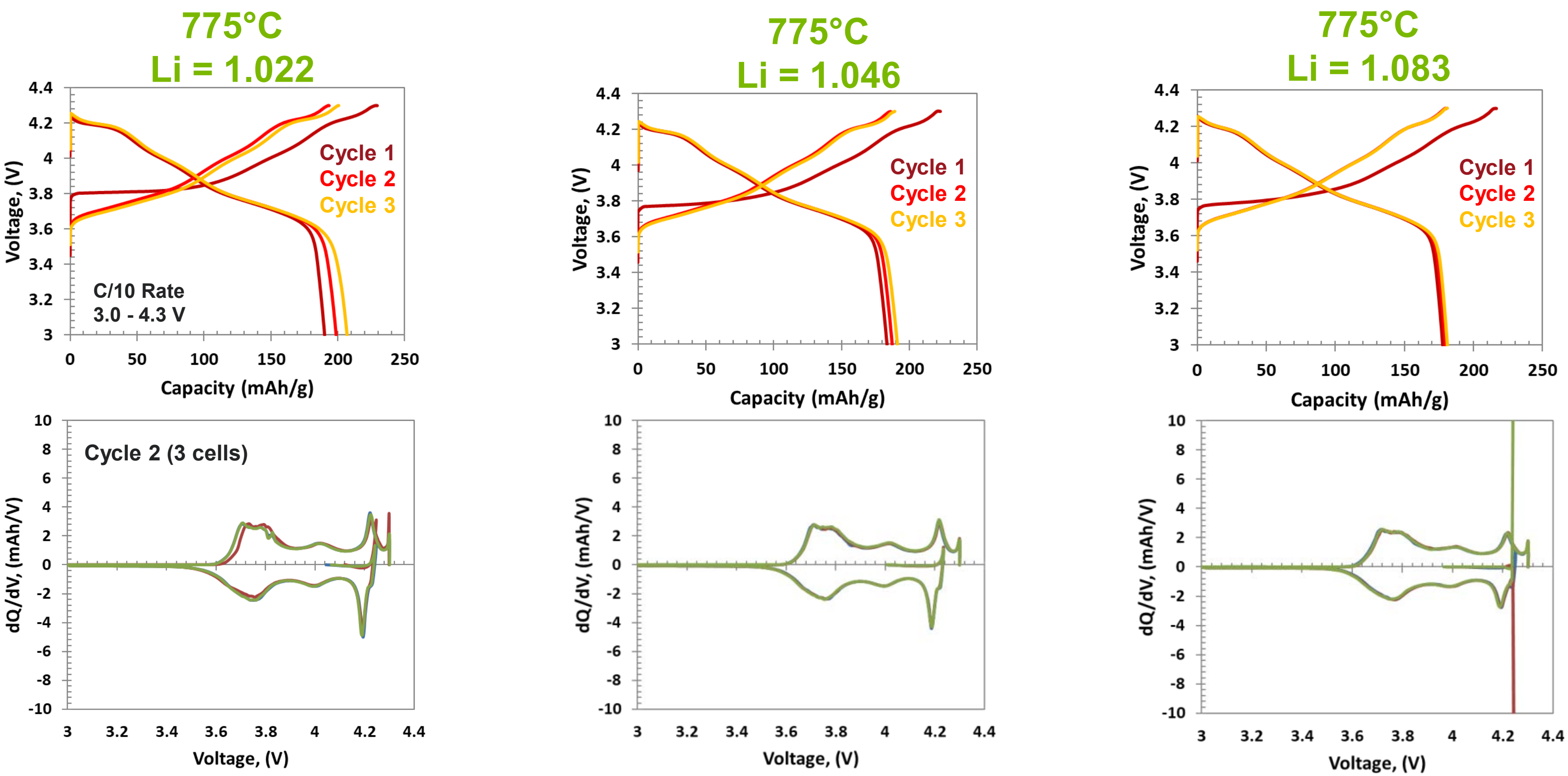
725°C
Li = 1.123





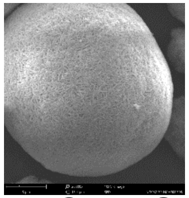
$LiNi_{0.9}Mn_{0.1}O_2$

Electrochemistry – 775°C Formation Cycles



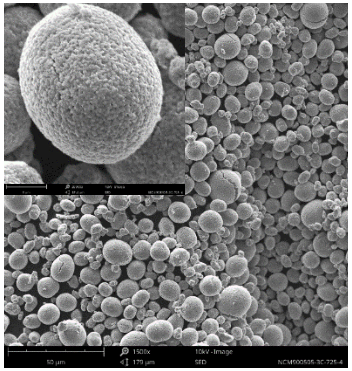
$LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ Calcination Optimization Studies

Former $\mathbf{Ni_{0.9}Co_{0.05}Mn_{0.05}(OH)_2}$ precursor; 1.98g/cc

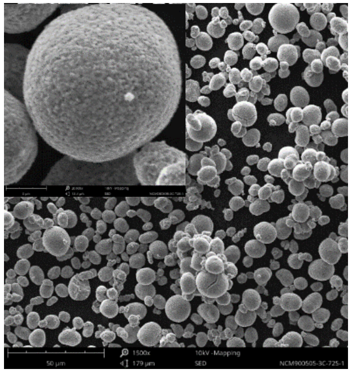


SEM – Cathode calcined at 725°C

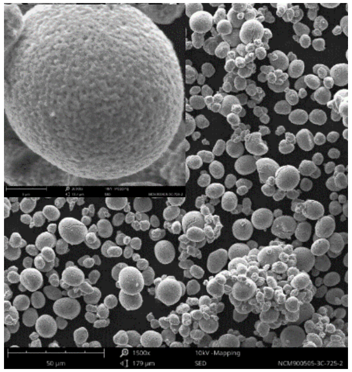
$Li_{1.005}Ni_{0.895}Mn_{0.051}Co_{0.053}O_2$



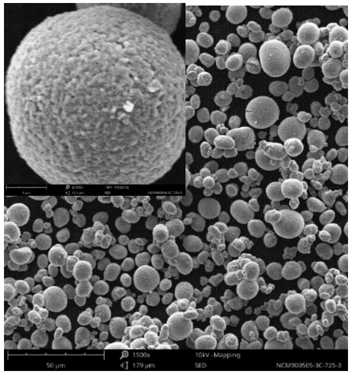
$Li_{1.067}Ni_{0.895}Mn_{0.051}Co_{0.053}O_2$



$Li_{1.106}Ni_{0.895}Mn_{0.051}Co_{0.053}O_2$

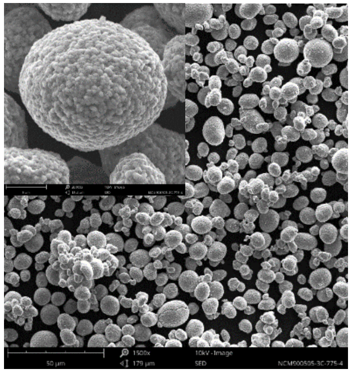


$Li_{1.154}Ni_{0.895}Mn_{0.051}Co_{0.053}O_2$

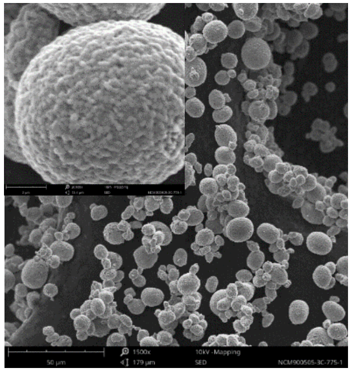


SEM – Cathode calcined at 775°C

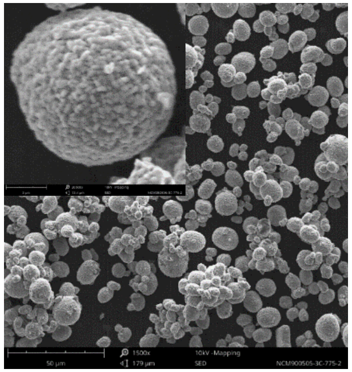
$Li_{0.991}Ni_{0.895}Mn_{0.051}Co_{0.053}O_2$



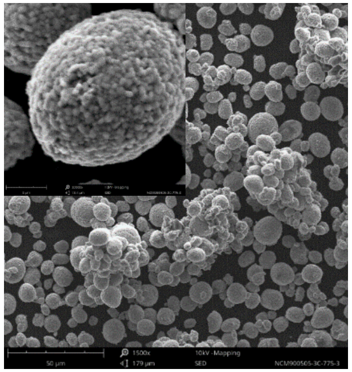
$Li_{1.057}Ni_{0.895}Mn_{0.051}Co_{0.053}O_2$



$Li_{1.093}Ni_{0.895}Mn_{0.051}Co_{0.053}O_2$

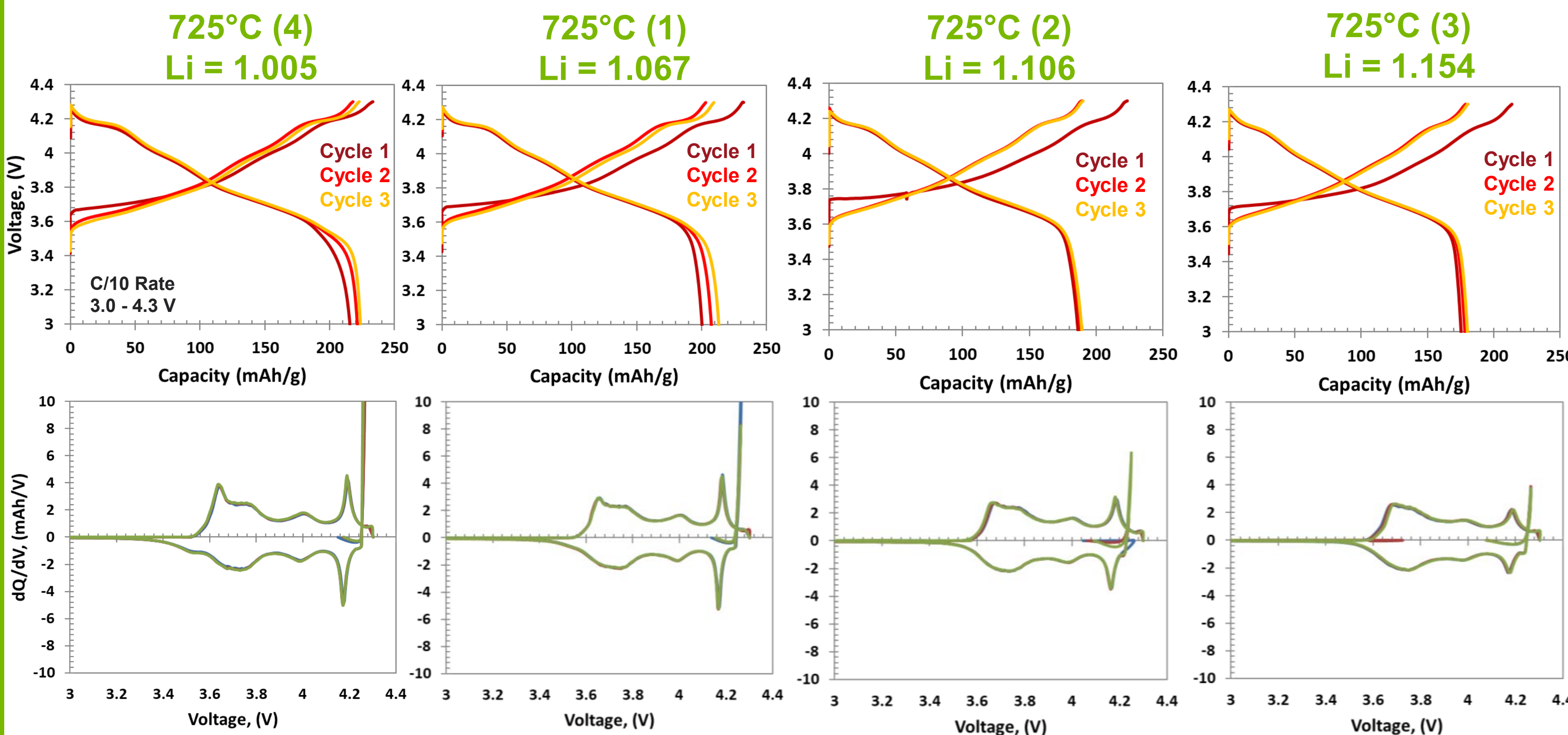


$Li_{1.113}Ni_{0.895}Mn_{0.051}Co_{0.053}O_2$



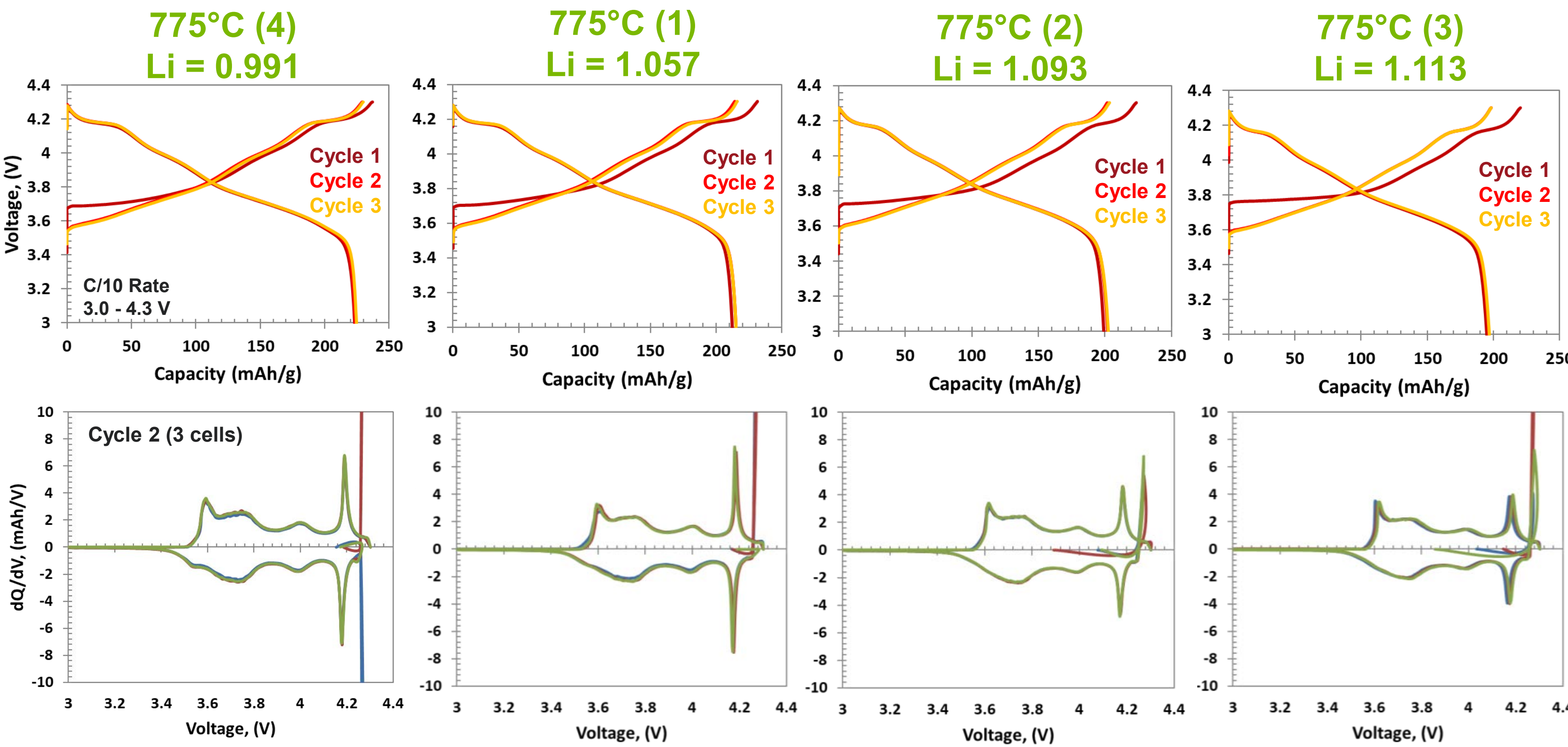
$LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$

Electrochemistry – 725°C Formation Cycles



$LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$

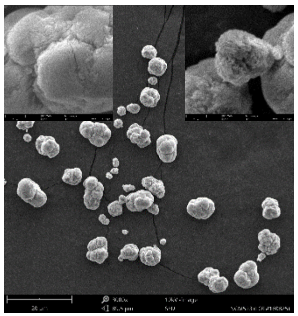
Electrochemistry – 775°C Formation Cycles



Single Crystal NCM523 Particles - Preliminary

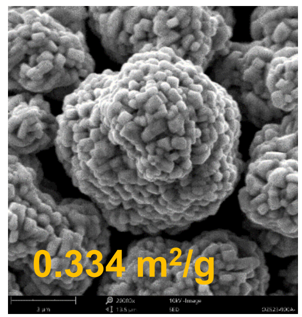
- Denser particles with higher degree of isolated crystals were prepared at high calcination temperatures using NMC hydroxide precursor with ~5-7 μm particle sizes made by TVR

Precursor

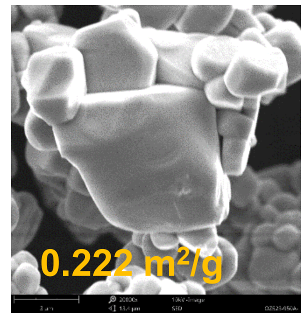


High temperature calcination

900°C

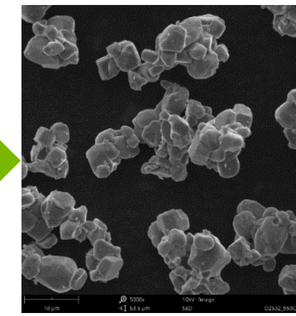


950°C

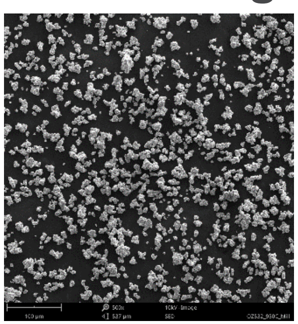


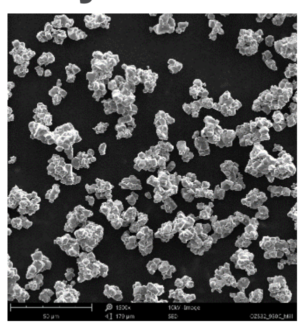
De-agglomeration

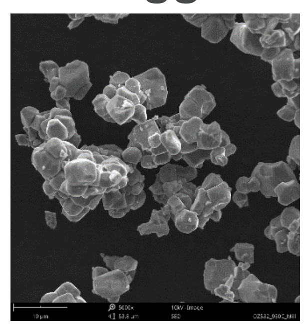
950°C

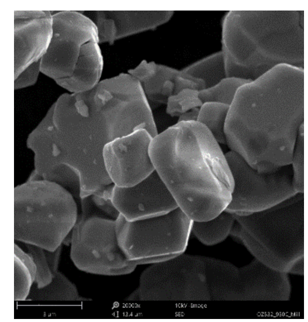


Resultant Single Crystals after De-agglomeration Process







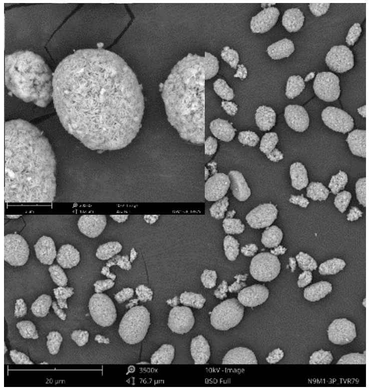


- 900°C is not hot enough to cause single crystal formation of NCM523
- Further calcination and de-agglomeration optimization is required

Single Crystal NCM811 Particles - Preliminary

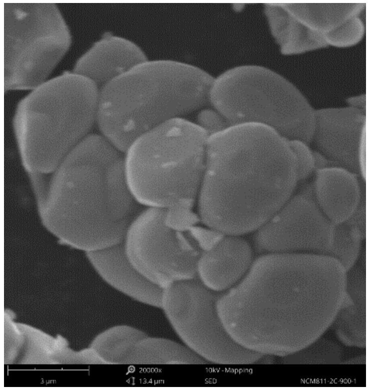
- Denser particles were prepared at high calcination temperatures using NMC811 hydroxide precursor with ~5 μm particle sizes made by TVR

Precursor

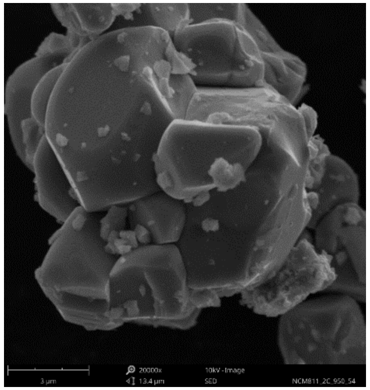


High temperature calcination

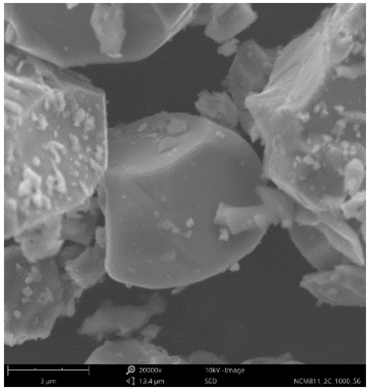
900°C



950°C



1000°C



- Target: Isolate the facet sharing crystals without damaging, as the calcination temperature goes high
- Further optimization will be focusing on controlling lithium ratio and calcination temperature and duration

AVAILABLE PRODUCTS & DELIVERIES MADE

DELIVERIES

- ~104g of $Ni(OH)_2$ (Lot #180823) : Chris Johnson (CSE, ANL)
- ~302g $Ni(OH)_2$ (Lot #180823) : Gabriel Veith (ORNL)
- ~0.1g $LiNiO_2$ (Lot#181107) : Fulya Dogan Key (CSE, ANL)
- ≥ 41g $LiNiO_2$ (Lot#181107) : Bryant Polzin (CSE, CAMP, ANL)
- ~40g NCM622 & 120g NCM811 & 20g LNO (<5 microns) : Volexion
- ~50g NCM622 & 50g NCM811 (≤5 microns) : Blue Current
- ~15 g each of → $Ni_{0.90}Mn_{0.10}(OH)_2$ & $Ni_{0.90}Co_{0.10}(OH)_2$ & $Ni_{0.90}Mn_{0.05}Co_{0.05}(OH)_2$: Gabriel Veith (ORNL)
- ~1 g $LiNi_{0.75}Mn_{0.25}O_2$ cathode: Fulya Dogan Key (CSE, ANL)

AVAILABLE PRODUCTS

- $Ni(OH)_2$ precursors:
  - Lot#180823: ~152g & Lot#180920: ~650g (fast TVR r x n)
  - Lot#181012: ~85g & Lot#181017: ~80g (standard TVR r x n)
  - Lot#190225: ~500g
- $Ni_{0.75}Mn_{0.25}(OH)_2$ precursor (by CSTR):
  - Lot#181205: ~600g
- $Ni_{0.90}Mn_{0.10}(OH)_2$ precursor (by TVR):
  - Lot#190115: ~500g
- $Ni_{0.90}Co_{0.10}(OH)_2$ precursor (by TVR):
  - Lot#190204: ~200g
- $Ni_{0.90}Mn_{0.05}Co_{0.05}(OH)_2$ precursor (by TVR):
  - Lot#190211: ~300g
- $Ni_{0.60}Mn_{0.20}Co_{0.20}(OH)_2$ precursor:
  - Lot#181024: ~90g (std TVR r x n)
- $Ni_{0.80}Mn_{0.10}Co_{0.10}(OH)_2$(10L TVR):
  - Lot#190312: ~700g (left)